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(54) End-capped polyfluorenes, films and devices based thereon

(57) The present invention relates to polyfluorenes end-capped with at least one charge-transporting moiety, and to films and devices based thereon.

Fig. 6

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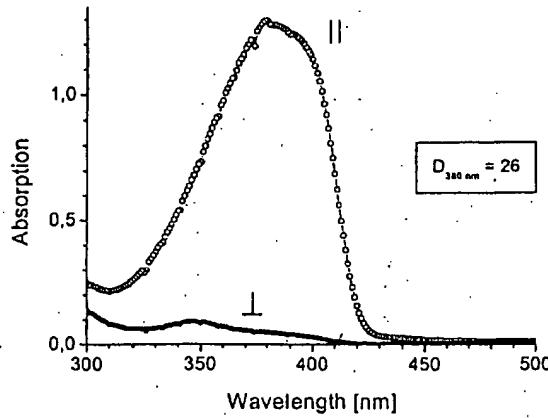
Description

[0001] The present invention relates to end-capped polyfluorenes, films and devices based thereon.

[0002] In recent years much attention has been paid to polymers being useful for incorporation into field-effect transistors, light-emitting diodes (LEDs) and photo-voltaic devices. A wide variety of polymers have been included as active media in these electronic devices. A class of compounds that has been found to be potentially useful for such purpose are the polyfluorenes.

[0003] Various reasons support the use of polyfluorenes in these devices: First of all, polyfluorenes are displaying impressive blue-emission properties and because of this they received considerable attention with respect to their potential for inclusion into emission layers of LEDs. Several reports have demonstrated bright blue emission from polyfluorene homopolymers (A.W. Grice; D. D. C. Bradley; M. T. Bernius; M. Inbasekaran; W. W. Wu; E. P. Woo; *Appl. Phys. Lett.* 1998, 73, 629; Y. Yang and Q. Pei; *J. Appl. Phys.* 81, 3294 (1997)).

[0004] A second important property of polyfluorenes, in particular polyfluorene homopolymers, is their thermotropic liquid-crystalline behaviour, which allows to orient these polymers on alignment layers, for example rubbed polyimide layers (M. Grell, D. D. C. Bradley, M. Inbasekaran, E. P. Woo, *Adv. Mater.* 9, 798 (1997); M. Grell, D. D. C. Bradley, X. Long, T. Chamberlain, M. Inbasekaran, E. P. Woo, M. Soliman, Acta Polym. 49, 439 (1998)). Orientation of the polymers on such alignment layers enables the emission of linearly polarized light which is particularly useful for devices such as liquid-crystal (LC) displays in which emission layers incorporating polyfluorene are being used as backlights. LEDs emitting linearly polarized light and having a dichroic ratio in emission of more than 20 and a brightness in excess of 100 cd/m^2 could be fabricated when the polyimide layers were doped with appropriate hole-transporting molecules (M. Grell, W. Knoll, D. Lupo, A. Meisel, T. Miteva, D. Neher, H. G. Nothofer, U. Scherf, H. Yasuda, Adv. Mater. 11, 671 (1999).

[0005] The efficiency of devices based on non-aligned and aligned polyfluorenes is, however, still far too low for applications. The efficiency of a bilayer device comprising a cross-linked hole-transporting layer (HTL) and an emission layer (EML) based on poly(9,9-bis(n-octyl)fluorene-2,7-diyl) (PFO) with linear octyl side-chains was only 0.25 cd/A (A. W. Grice; D. D. C. Bradley; M. T. Bernius; M. Inbasekaran; W. W. Wu; E. P. Woo; *Appl. Phys. Lett.* 73, 629 (1998)). Devices with aligned polyfluorenes, using poly(9,9-bis(2-ethylhexyl)fluorene-2,7-diyl) are reported to show an even lower efficiency of approximately 0.12 cd/A (M. Grell, W. Knoll, D. Lupo, A. Meisel, T. Miteva, D. Neher, H. G. Nothofer, U. Scherf, H. Yasuda, Adv. Mater. 11, 671 (1999)).

[0006] Several attempts have been made to chemically modify polyfluorenes in order to increase the device efficiency. For example Kim et al. (Macromolecular Symposia, 1999, 143, 221-230) copolymerized 2,7-diethynyl-9,9'-di-n-hexylfluorene and 2,7-dibromo-9,9'-di-n-hexylfluorene to yield poly(9,9'-di-n-hexyl-2,7-fluorenyleneethynylene). The alternating copolymer emitted blue colour with a peak maximum at 475 nm on excitation either at 340, 365 or 400 nm. The principle emission maximum shifted to 425 nm on excitation at 340 nm when the polymer was blended with polyvinylcarbazole (PVK). Light-emitting diodes (LEDs) fabricated with the alternating copolymer sandwiched between indium-tin oxide glass and Al emitted a light with a peak maximum at 550 nm. The peak maximum shifted to 425 nm when the copolymer was blended with PVK with the blending ratios between 5 to 20 % of the emissive copolymer.

[0007] Colour tuning was deliberately achieved via incorporation of benzothiadiazole, perylene or anthracene moieties (Klaerner, G.; Davey, M. H.; Chen, W. D.; Scott, J. C.; Miller, R. D.; *Adv. Mater. 10*, 993 (1998); M. Kreyenschmidt, G. Klärner, T. Fuhrer, J. Ashenhurst, S. Karg, W. D. Chen, V. Y. Lee, J. C. Scott, R. D. Miller, *Macromolecules 31*, 1099 (1998); Y. He, S. Gong, R. Hattori, J. Kanicki, *Appl. Phys. Lett. 74*, 2265 (1999)). The problem, however, with the inclusion of such chemical moieties into the polyfluorene main chain or the copolymerization with other monomers is the inevitable modification of essential properties of the main chain such as the stiffness and the geometrical shape, thereby inadvertently altering the character of the polyfluorene, e. g. its liquid-crystalline behaviour, if such had been present before any modification.

[0008] Another problem with LED-devices based on polyfluorene emission layers is that the emission spectrum of such an LED exhibits a significant contribution of longer wavelengths, particularly in the range of the red part of the spectrum (M. Grell, D. D. C. Bradley, X. Long, T. Chamberlain, M. Inbasekaran, E. P. Woo, M. Soliman; *Acta Polym.* 49, 439 (1998); M. Grell, W. Knoll, D. Lupo, A. Meisel, T. Miteva, D. Neher, H. G. Nothofer, U. Scherf, H. Yasuda, Adv. Mater. 11, 671 (1999); J. Teetsov, M. A. Fox; *Journal of Materials Chemistry 9*, 2117 (1999), V. N. Bliznyuk, S. A. Carter, J. C. Scott, G. Klärner, R. D. Miller, and D. C. Miller; *Macromolecules 32*, 361 (1999)). The strength of this contribution changes strongly with the molecular weight and the nature of the side chains. This situation is aggravated by the fact that the alignment of the polymer in the liquid-crystalline state requires an annealing step at higher temperatures enhancing this undesired red contribution. Several attempts have been made towards a control of red-shifted emission bands. These include the synthesis of statistical (M. Kreyenschmidt, G. Klärner, T. Fuhrer, J. Ashenhurst, S. Karg, W. D. Chen, V. Y. Lee, J. C. Scott, R. D. Miller; *Macromolecules* 1998, 31, 1099) or block (D. Marsitzky, M. Klapper, K. Müllen; *Macromolecules* 1999, 32, 8685) copolymers, the attachment of sterically demanding groups (G. Klärner, R. D. Miller, C. J. Hawker; *Polym. Prepr. 1998*, 1006) or thermal cross-linking of terminal reactive groups, e. g. benzocy-

clobutane ((a) E. P. Woo, M. Inbasekaran, W. Shiang, G. R. Roof; *Int. Pat. Appl. WO97/05184* (1997); (b) M. Inbaseka-ran, W. Wu, E. P. Woo; *US Pat.* 5,770,070 (1998)) units or unsaturated functions (e. g. styryl) (Klaerner, G.; Davey, M. H.; Chen, W. D.; Scott, J. C; Miller, R. D.; *Adv. Mater.* 1998, *10*, 993; G. Klärner, J.-I. Lee, V. Y. Lee, E. Chan, J.-P. Chen, A. Nelson, D. Markiewitz, R. Siemens, J. C. Scott, R. D. Miller; *Chem. Mater.* 1999, 11, 1800). In most of these cases the electronic properties as well as the phase behaviour have become severely altered compared to that of the polyfluorene homopolymers. For example the synthesis of block copolymers has in fact led to an even increased contribution of undesired red-shifted emission states (D. Marsitzky, M. Klapper, K. Müllen; ibid.).

[0009]   Accordingly, it is an object of the present invention to provide polymers useful for incorporation into electronic devices such as FETs, LEDs and photovoltaic devices which do not show any unwanted red-shift contribution. Partic-ularly it is an object of the present invention to provide polyfluorenes useful for incorporation into these devices which do not show any undesired red-shift contribution. Another object of the present invention is to provide polymers, in particular polyfluorenes, that allow for the fabrication of electronic devices, in particular LEDs, FETs and photovoltaic devices with a higher efficiency. It is another object of the present invention to provide LEDs with a higher brightness, a lower onset voltage, a negligible red contribution, a better colour stability and the potential to achieve high dichroic ratios.

[0010]   All these objects are solved by a polyfluorene end-capped with at least one charge-transporting moiety.

[0011]   It is preferred that in such a polyfluorene the charge-transporting moiety is selected from the group comprising electron-transporting moieties, hole-transporting moieties and ion-transporting moieties, wherein, more preferably, the charge-transporting moiety is selected from the group comprising :
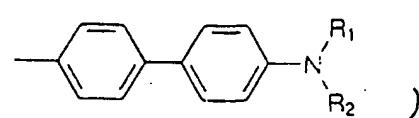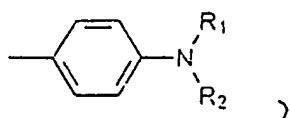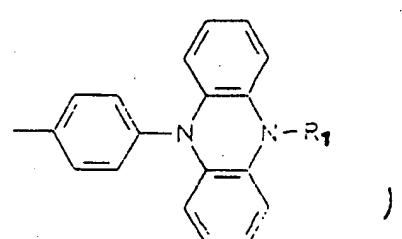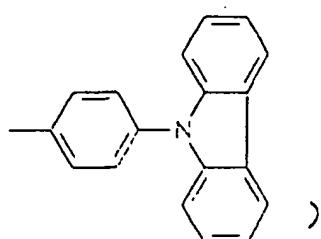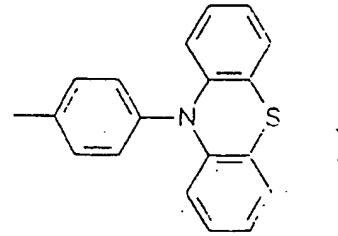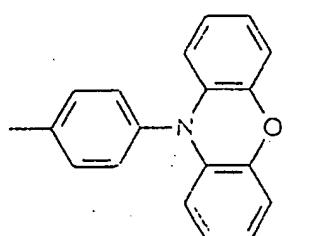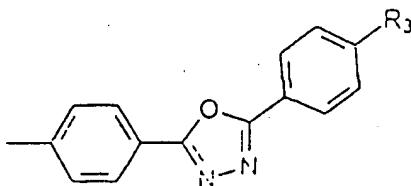
wherein R_1 and R_2 are independently at each occurrence selected from the group comprising straight chain C_{1-20} alkyl, branched C_{1-20} alkyl, aryl, substituted aryl, alkylaryl, substituted alkylaryl, alkoxyaryl, substituted alkoxyaryl, aryloxyaryl, substituted aryloxyaryl, dialkylaminoaryl, substituted dialkylaminoaryl, diarylaminoaryl and substituted diarylaminoaryl, and

wherein R_3 is independently at each occurrence selected from the group comprising straight chain C_{1-20} alkyl, branched C_{1-20} alkyl, aryl, substituted aryl, alkylaryl and substituted alkylaryl.

[0012] In one embodiment it is preferred that the polyfluorene comprises about 0.5 - 9 percent by weight of charge-transporting moieties.

[0013] It is also preferred that the polyfluorene comprises about 0.5 - 9 mole percent of charge-transporting moieties.

[0014] In a particularly preferred embodiment R_1 and R_2 are independently at each occurrence selected from the group comprising 4-methylphenyl, 2-methylphenyl, phenyl, 1-naphthyl, 2-naphthyl, 4-methoxyphenyl, 2-methoxyphenyl, 4-dimethylaminophenyl, 2-dimethylaminophenyl, 4-diphenylaminophenyl and 4-phenoxyphenyl.

[0015] Preferred combinations are:

a) R_1 = phenyl, R_2 = 4-methylphenyl;
b) R_1 = phenyl, R_2 = 1-naphthyl;
c) R_1 = phenyl, R_2 = 2-naphthyl;
d) R_1 = R_2 = 4-methylphenyl;
e) R_1 = R_2 = phenyl;
f) R_1 = R_2 = 4-dimethylaminophenyl;
g) R_1 = R_2 = 4-diphenylaminophenyl.

[0016] The objects of the invention are also solved by a polyfluorene end-capped with at least one moiety selected from the group comprising

wherein R_1 and R_2 are independently at each occurrence selected from the group comprising straight chain C_{1-20} alkyl, branched C_{1-20} alkyl, aryl, substituted aryl, alkylaryl, substituted alkylaryl, alkoxyaryl, substituted alkoxyaryl, aryloxyaryl, substituted aryloxyaryl, dialkylaminoaryl, substituted dialkylaminoaryl, diarylaminoaryl and substituted diarylaminoaryl, and

wherein R_3 is independently at each occurrence selected from the group comprising straight chain C_{1-20} alkyl, branched C_{1-20} alkyl, aryl, substituted aryl, alkylaryl and substituted alkylaryl.

[0017] In one embodiment it is preferred that the polyfluorenc comprises about 0,5 - 9 percent by weight of charge-transporting moieties.

[0018] It is also preferred that the polyfluorene comprises about 0,5 - 9 mole percent of charge-transporting moieties.

[0019] In a preferred embodiment R_1 and R_2 are independently at each occurrence selected from the group comprising 4-methylphenyl, 2-methylphenyl, phenyl, 1-naphthyl, 2-naphthyl, 4-methoxyphenyl, 2-methoxyphenyl, 4-dimethylaminophenyl, 2-dimethylaminophenyl, 4-diphenylaminophenyl and 4-phenoxyphenyl.

[0020] Preferred combinations are:

a) R_1 = phenyl, R_2 = 4-methylphenyl;
b) R_1 = phenyl, R_2 = 1-naphthyl;
c) R_1 = phenyl, R_2 = 2-naphthyl;
d) R_1 = R_2 = 4-methylphenyl ;
e) R_1 = R_2 = phenyl;
f) R_1 = R_2 = 4-dimethylaminophenyl;
g) R_1 = R_2 = 4-diphenylaminophenyl.

[0021] The objects of the present invention are further solved by a polyfluorene having the formula
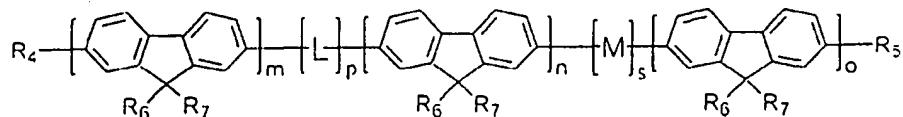
wherein R_4 and R_5 are independently at each occurrence selected from the group comprising:

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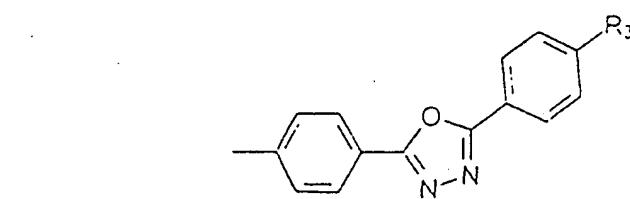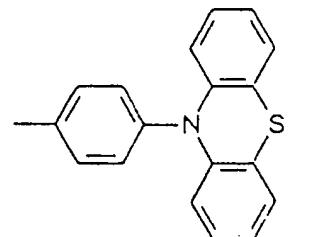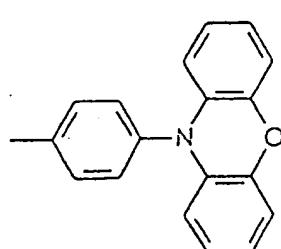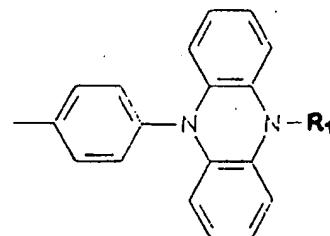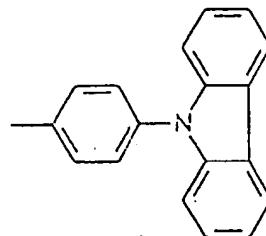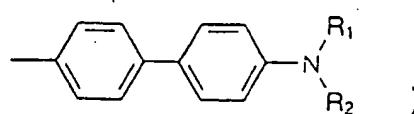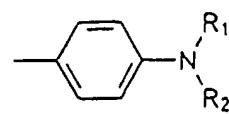
45   and H,

R$_1$ and R$_2$ being independently selected from the group comprising straight chain C$_{1-20}$ alkyl, branched C$_{1-20}$ alkyl, aryl, substituted aryl, alkylaryl, substituted alkylaryl, alkoxyaryl, substituted alkoxyaryl, aryloxyaryl, substituted aryloxyaryl, dialkylaminoaryl, substituted dialkylaminoaryl, diarylaminoaryl and substituted diarylaminoaryl,

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R$_3$ being selected from the group comprising straight chain C$_{1-20}$ alkyl, branched C$_{1-20}$ alkyl, aryl, substituted aryl, alkylaryl and substituted alkylaryl,

and wherein R$_6$ and R$_7$ are independently at each occurrence selected from the group comprising straight chain C$_{1-20}$
55   alkyl, branched chain C$_{1-20}$ alkyl, aryl, substituted aryl, alkylaryl, substituted alkylaryl, -(CH$_2$)$_q$-(O-CH$_2$-CH$_2$)$_r$-O-CH$_3$,
         q being selected from the range 1≤q≤10, r being selected from the range 0≤r≤20,
and wherein L and M are independently at each occurrence selected from the group comprising thiophene, substituted thiophene, phenyl, substituted phenyl, phenanthrene, substituted phenanthrene, anthracene, substituted anthracene,

any aromatic monomer that can be synthesized as a dibromo-substituted monomer, benzothiadiazole, substituted benzothiadiazole, perylene and substituted perylene,

and wherein m+n+o≥10, each of m, n, o being independently selected from the range 1 - 1,000,

and wherein p is selected from the range 0 - 15,

and wherein s is selected from the range 0 - 15,

with the proviso that, if R_4 is H, R_5 is not H, and if R_5 is H, R_4 is not H.

[0022] In one embodiment a polyfluorene is preferred,

wherein m, p, s, o are 0, and

wherein R_4 - R_7 and R_1 - R_3 are as previously defined.

[0023] In one embodiment a polyfluorene is preferred which comprises about 0.5 - 9 percent by weight of R_4- and R_5-groups.

[0024] In one embodiment a polyfluorene is preferred which comprises about 0.5 - 9 mole percent of R_4- and R_5-groups.

[0025] It is preferred that a polyfluorene according to the present invention be cross-linked to a polyfluorene according to the present invention via at least one linkage selected from the group comprising a 9,9-spirobifluorene-linkage, a bifluorenyl-linkage, a bifluorenylidene-linkage and an α,ω-difluorenylalkane-linkage with a length of the alkane spacer in the range from 1 - 20 C-atoms.

[0026] It is also preferred that a polyfluorene according to the present invention has at least one color-tuning moiety incorporated into the main chain, wherein, more preferred, the color-tuning moiety is selected from the group comprising thiophene, substituted thiophene, phenyl, substituted phenyl, phenanthrene, substituted phenanthrene, anthracene, substituted anthracene, any aromatic monomer that can be synthesized as a dibromo-substituted monomer, benzo-thiadiazole, substituted benzothiodiazole, perylene and substituted perylene.

[0027] In one embodiment a polyfluorene is preferred which is liquid-crystalline, wherein, more preferred, it is liquid-crystalline at or above 70°C.

[0028] In another embodiment a polyfluorene is preferred, which is amorphous.

[0029] The objects of the present invention are furthermore solved by a polyfluorene selected from the group comprising
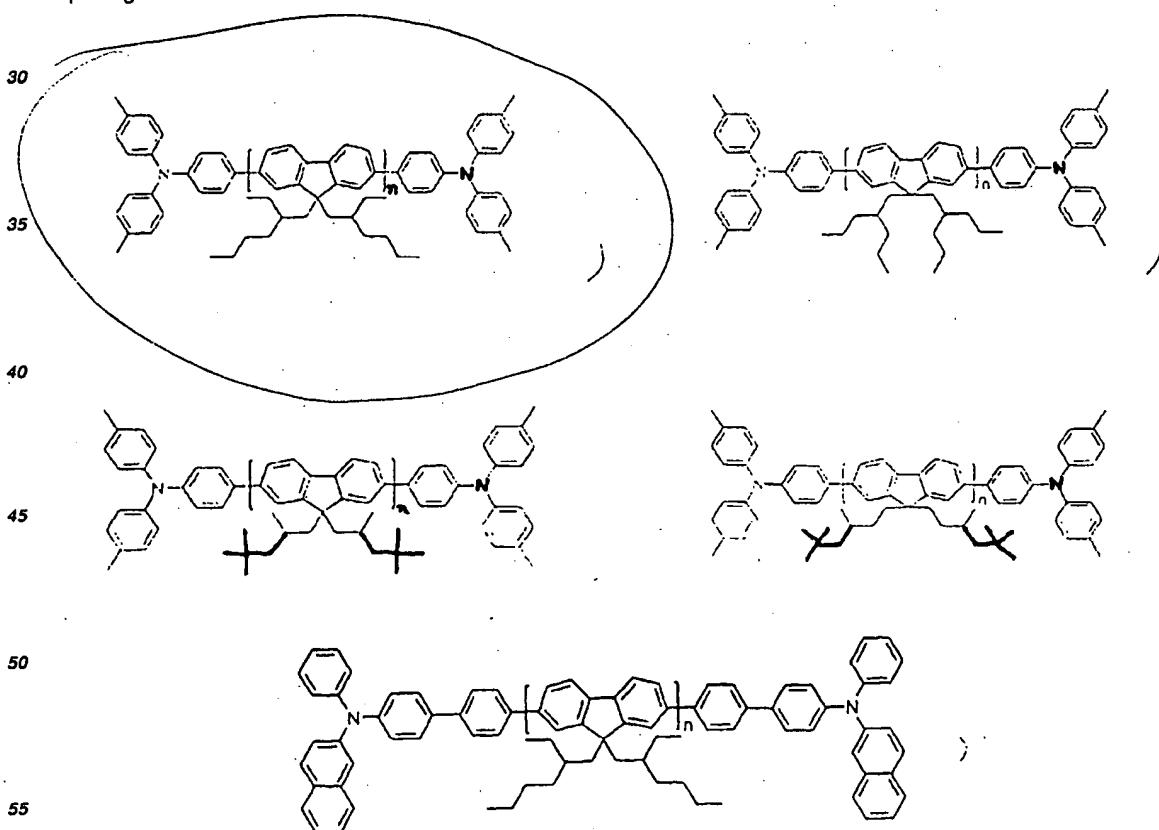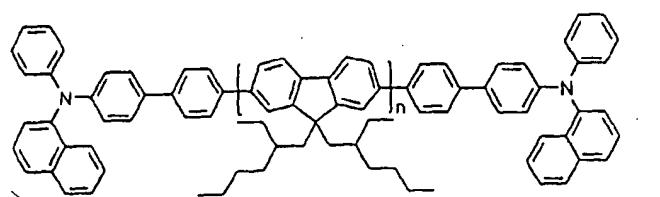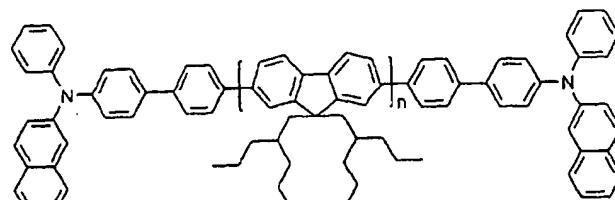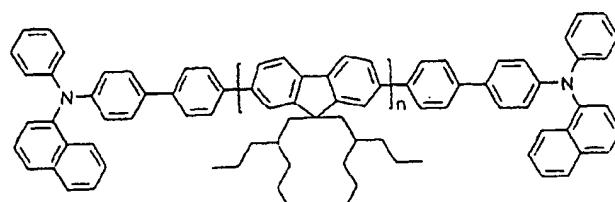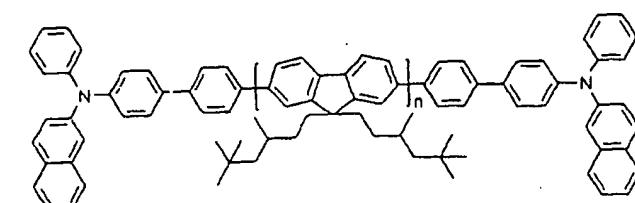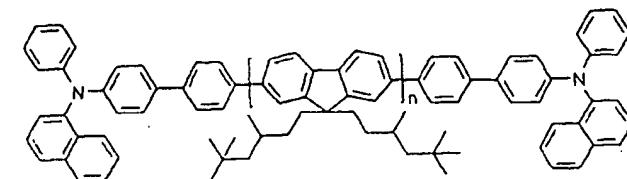
wherein n is as previously defined.

[0030]   The objects of the present invention are also solved by a film incorporating a polyfluorene according to the present invention.

[0031]   It is preferred that the film be aligned.

[0032] It is preferred that the film incorporates at least one other substance, wherein said other substance is selected from the group comprising fluorescent dyes, hole-transporting moieties, electron-transporting moieties, ion-transporting moieties, phosphorescent dyes, nanoparticles, low molecular weight liquid-crystalline moieties, other liquid-crystalline and/or fluorescent and/or phosphorescent and/or charge-transporting polymers.

[0033] In one embodiment it is preferred that the film be deposited on an alignment layer.

[0034] In one embodiment the film has a thickness ranging from 10 nm to 2 μm. In one embodiment it is preferred that the film has a thickness ranging from 50 - 300 nm.

[0035] The objects of the present invention are also solved by a device selected from the group comprising FETs, photovoltaic elements, LEDs and sensors, incorporating a polyfluorene according to the present invention.

[0036] It is preferred that the device has another polymer incorporated, wherein, more preferred, said polymer is a luminescent polymer.

[0037] The objects of the present invention are also solved by a device selected from the group comprising FETs, photovoltaic elements, LEDs and sensors, incorporating a film according to the present invention.

[0038] The objects of the present invention are also solved by the use of a polyfluorene according to the present invention in a film, wherein, more preferred, the film is an emission layer.

[0039] The objects of the present invention are also solved by the use of a polyfluorene according to the present invention in a device selected from the group comprising FETs, photovoltaic elements, LEDs and sensors.

[0040] The objects of the present invention are also solved by the use of a film according to the present invention in a device selected from the group comprising FETs, photovoltaic elements, LEDs, and sensors.

[0041] The objects of the present invention are also solved by the use of a device according to the present invention in combination with a liquid-crystal display (LCD).

[0042] It has surprisingly been found that end-capping a polyfluorene polymer main chain with charge-transporting moiety yields LEDs with a higher efficiency and a better colour stability, yet without altering the electronic properties of the polyfluorene polymer main chain. Furthermore, surprisingly, end-capping with appropriate charge-transporting groups does not disturb the phase property of the polyfluorene polymer and does not influence their orientational capabilities. A further advantage in connection with the present invention is the fact that end-capping the polyfluorene molecule with a charge-transporting moiety in the indicated weight-percent range or mole-percent range enables a precise control of the molecular weight of the polyfluorene.

[0043] The terms as used herein are defined as follows:

[0044] A molecule is "end-capped with" a group if the group is attached, preferably, covalently attached, to said molecule. The site of attachment can be any site in the molecule that renders the attached group a terminal group; in the case of a linear polymer the preferred site of end-capping are the two termini. Attachment-sites, however, other than the terminal sites are envisaged, too, such as attachment-sites for side chains. In a branched polymer the preferred sites for end-capping are the terminal sites of each branch of the polymer.

[0045] The term "charge-transporting moiety" is meant to designate any chemical moiety capable of facilitating the transport of electrons, holes (e. g. charge-deficiencies, particularly electron-deficiencies) and ions. The term furthermore comprises also those groups, that can be transformed into electron-transporting moieties, hole-transporting moieties or ion-transporting moieties, e. g. by protonation, cleavage, proteolysis, photolysis etc.

[0046] A "colour-tuning moiety" is any moietiy capable of modifying the spectral properties of a molecule to which such moiety is attached and/or into which such moiety is incorporated.

[0047] A "film" is any layer having a thickness selected from the range 10 nm - 2 μm, preferably selected from 50 - 300 nm. Such a film can, e. g., be an emission layer of an opto-electronic device, e. g. an LED. The film can be aligned or non-aligned and prepared by, for example, casting from solution, spin casting, doctor-blading, offset printing, inkjet printing etc. The alignment is preferably achieved by annealing through heating above or close to the transition temperature to the liquid-crystalline phase, but other methods and ways of annealing and aligning are possible, for example by exposition to solvent vapor. The film can be deposited on a specific alignment layer for the purpose of alignment of the molecules in the film, or it can be aligned directly by techniques such as stretching, rubbing etc. Preferable materials for an alignment layer are selected from the group comprising polyimide, nylon, PVA, poly(p-phenylene vinylene), polyamide, teflon (hot rubbed) and glass, but are not restricted thereto. The alignment layer can have its properties induced by rubbing, illumination with polarized light, ion-bombardment, surface-structure induction by grating etc.. In a device according to the present invention a film according to the present invention can be used in conjunction with at least one other layer, e. g. another emission layer or several other emission layers, depending on the requirements of the application (in addition to the other layers whose presence is inherently essential for the proper functioning of the device).

[0048] The term "in combination with a liquid-crystal display" is meant to designate any arrangement in which a film and/or a device according to the present invention is in physical proximity to a liquid-crystal display (LCD) and/or functionally coupled thereto, e. g. the use of an LED, preferably an LED emitting polarized light, as a backlight for a liquid-crystal display.

[0049] The invention is now being described more fully in the following specific description and the following figures, wherein

Fig. 1 shows a general synthetic route to poly(9,9-dialkylfluorene-2,7-diyl)s;

Fig. 2 shows luminance-voltage curves for LEDs with emission layers of pure poly(2,7-(9,9-bis(2-ethylhexyl))fluorene (PF2/6_1) and poly(2,7-(9,9-bis(2-ethylhexyl))fluorene)-2,7-bis(4-methylphenyl)phenylamine end-capped with different concentrations (2, 4, 9 mol%) of the hole-transporting end-capper (PF2/6am2, PF2/6am4; PF2/6am9); the inset of Fig. 2 shows luminescence-current density curves for the same devices;

Fig. 3 shows normalized electroluminescence spectra of the devices with active layers of pure poly(2,7-(9,9-bis (2-ethylhexyl)fluorene (PF2/6_1 & PF 2/6_2) with different molecular weights and poly(2,7-(9,9-bis(2-ethylhexyl)) fluorene)-2,7-bis(4-methylphenyl)phenylamine (PF2/6am2; PF2/6am4; PF2/6am9) with different concentrations of the hole-transporting end-capper;

Fig. 4 shows luminance-voltage curves for LEDs with emission layers of pure poly(9,9-bis(2,4,4-trimethylpentyl) fluorene (PF3/1/5) and poly(9,9-bis(2,4,4-trimethylpentyl)fluorene-2,7-bis-(4-methylphenyl)phenylamine (PF3/1/5am4) end-capped with 4 mol% end-capper; the inset shows normalized electroluminescent spectra of the same devices;

Fig. 5 shows luminance-voltage curves for LEDs with emissive layers of pure poly(2,7-(9,9-bis(2-propylpentyl)) fluorene (PF3/5) and poly(2,7-(9,9-bis(2-propylpentyl))fluorene-2,7-bis(4-methylphenyl)phenylamine (PF3/5am6) end-capped with 6 mol% end-capper; the inset shows normalized electroluminescent spectra of the device with end-capped polymer fresh and after 15 minutes of operation;

Fig. 6 shows the polarized absorption of a ca. 100 nm thick aligned layer of poly(2,7-(9,9-bis(2-ethylhexyl))fluorene-2,7-bis(4-methylphenyl)phenylamine (PF2/6am4) with 4 mol% end-capper on rubbed polyimide annealed at 145° under Argon;

Fig. 7 shows an intensity-voltage curve for a polarized LED with an aligned poly(2,7-(9,9-bis(2-ethylhexyl))fluorene-2,7-bis(4-methylphenyl)phenylamine (PF2/6am4), 4 mol% end-capper, emission layer; the inset shows emission spectra of the same device measured parallel and perpendicular to the rubbing direction of the hole-transporting layer.

[0050] The following non-limiting examples describe the present invention more fully and in a more detailed manner without being intended to limit the present invention.

Examples:

Example 1: Synthesis of monomers

[0051] The synthesis of high molecular weight, soluble polyfluorenes by transition metal catalyzed aryl-aryl coupling was firstly described by Pei and Yang from UNIAX Corp. (Y. Yang, Q. Pei; J. Am. Chem. Soc., 118, 7416 (1996)). The materials used for device fabrication were synthesized according to general procedures for Yamamoto-type reductive polycondensations of dihaloaromatic compounds with Ni(COD)$_2$ as an effective aryl-aryl coupling agent (T. Yamamoto; Progr. Polym. Sci., 17, 1153 (1992)). The 9,9-dialkyl-substituted monomers were prepared in close analogy to literatures methods ((a) E. P. Woo, M. Inbasekaran, W. Shiang, G. R. Roof; Int. Pat. Appl. WO97/05184 (1997); (b) M. Inbasekaran, W. Wu, E. P. Woo; US Pat. 5,777,070 (1998)). Where required, a primary alcohol was converted into the corresponding alkylbromide prior to the alkylation of 2,7-dibromofluorene.

Example 2: Synthesis of end-capped polymers

[0052] At the beginning bis(4-methylphenyl)(4-bromophenyl)amine was added to the reaction mixture at a concentration of 2-9 mol/l as a suitable monofunctional end capping reagent to the reaction mixture. The resulting polymers were precipitated in a mixture of methanol/acetone/conc. hydrochloric acid and extracted with ethylacetate for 5 days. Finally the polymers were redissolved in toluene, the solvent partially evaporated, the polymers reprecipitated and dried in vacuum at 80°C. Yields are between 50 % - 80 %.

[0053] The monofunctionality of the end-capping reagent ensured that the polymer was terminated upon reaction

with such reagent. According to this synthetic procedure none of the end-capping moieties will therefore be incorporated into the bulk of the main chain. Instead the end-capping moiety will come to lie exclusively at the termini of the polymer.

[0054]   The following polymers were prepared according to this procedure:

Poly(2,7-(9,9-bis(2-ethylhexyl))fluorene)-2,7-bis(4-methylphenyl)phenylamine [PF2/6am]:
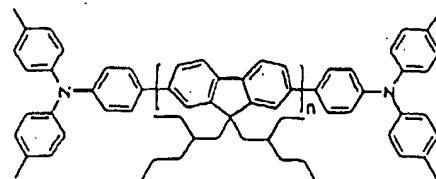
Poly(2,7-(9,9-bis(2-propylpentyl))fluorene)-2,7-bis(4-methylphenyl)phenylamine) [PF3/5am]:
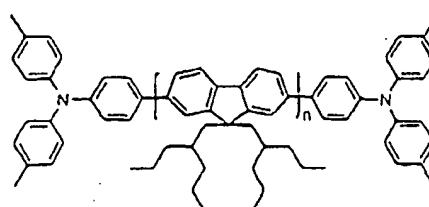
Poly(9,9-bis(2,4,4-trimethylpentyl)fluorene)-2,7-bis(4-methylphenyl)phenylamine [PF3/1/5am]:
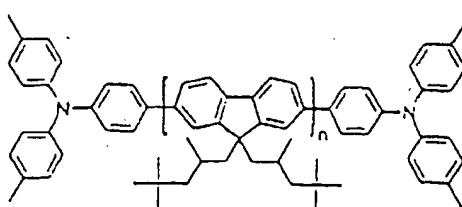
Poly(9.9-bis(3,5.5-trimethylhexyl)fluorene)-2,7-

bis(4-methylphenyl)phenylamine [PF3/1/6am]:
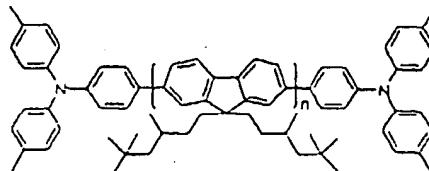
[0055] Summary of investigated end capped polyfluorenes. Gel-permeation chromatography (GPC) was carried out in THF with polystyrene standard:

|	Ratio Monomer : End Capper (in the beginning of polymerization reaction)	M_n (g/mol)	M_w (g/mol)	D
PF2/6am2	98:2	102000	145000	1,42
PF2/6am4	96:4	48400	75100	1,55
PF2/6am9*	91:9	12000	30800	2,57
PF3/5am6	94:6	29500	54300	1,84
PE3/1/5am4	96:4	32000	61500	1,92
PF3/1/6am2	98:2	70800	137300	1,94

*The polymer was extracted with acetone instead of ethylacetate.

Example 3: Fabrication of LED Devices

[0056] Single layer LEDs were prepared from the pure PF2/6 and from PF2/6 end-capped with 2, 4 and 9 mol% triphenylamine - PF2/6am2, PF2/6am4 and PF2/6am9, respectively. Pure PF3/5 and end-capped PF3/5am, as well as pure PF3/1/5 and end-capped PF3/1/5am were also investigated. All devices were fabricated at ambient conditions by spin-casting the polymer solution in toluene onto glass substrates covered by patterned ITO electrodes and a 25 nm layer of the conducting polymer polyethylenedioxythiophene (PEDT). Samples were dried in vacuum at room temperature for 24 hours prior to evaporation of Ca/Al top electrodes. Typical emission layer thicknesses (as measured with a Tencor α-step profiler) were 90 nm. The overlap between the two electrodes resulted in device areas of 5 mm^2. The device characterization was carried out in an evacuated sample chamber.

Example 4: Device Characteristics of LEDs based on PF2/6am

[0057] The luminance-voltage curves of the devices with active layers of PF2/6am2, PF2/6am4, and PF2/6am9 are shown in Fig. 2. Also displayed are the device characteristics of a device with the emission layer based on non end-capped polyfluorene (PF2/6_1, M_n = 195 000). The brightness at 9 V increases from ca. 50 cd/m^2 for the non end-capped polymer up to 1500 cd/m^2 for the PF2/6 with 9 mol% end-capper. The insert plot shows the increase in efficiency with increasing end-capper concentration - up to ca. 0.4 Cd/A at 1500 cd/m^2 for the device with the highest end-capper content. The deviations for the sample with 4 mol% end-capper could be due to the higher degree of crystallinity of the emission layer formed by this polymer.

Example 5: Spectral Characteristics of LEDs based on PF2/6am

[0058] Emission spectra were recorded on a E686 Princeton Applied Research Model 1235 digital triple grating spectrograph for devices with emission layers based on PF2/6am2, PF2/6am4, PF2/6am9, PF2/6_1 and a homopol-

ymer with a molecular weight M_n = 100 000 (PF2/6_2). Three main peaks can be identified in the PF EL-spectrum shown in Fig. 3: exciton emission at ca. 422 nm and 448 nm (zero phonon line and its vibronic progression) and a broad band at ca. 517 nm. For the pure PF2/6 with a higher molecular weight (PF2/6_1) the EL spectrum is entirely governed by the red-shifted emission at ca. 520 nm, with significant variations from sample to sample. The hole-transporting end-capper (HTE) content significantly affects the EL spectra of PF2/6am as shown in Fig. 3. Upon increasing the end-capper concentration, the intensity of the vibronic progression becomes smaller and the red contribution at 517 nm is fully suppressed. It is to be noted that PF2/6am2 with 2 mol% hole-transporting end-capper has approx. the same M_n as the non-end-capped PF2/6_2.

Example 6: Device Characteristics and Spectral Properties of LEDs based on PF3/1/5am

[0059]   Similar effects are observed for the polyfluorene with symmetrical but bulky side-chain pattern (PF3/1/5) as shown in Fig. 4. Upon end-capping with 4 mol% HTE, the onset voltage for electroluminescence becomes smaller and the device brightness increases. The blue excitonic emission band at 422 nm representing the inherent characteristics of polyfluorenes becomes more pronounced and the red contribution at ca. 517 nm is strongly suppressed. The M_n of the non-end-capped PF3/1/5 was 80 000.

Example 7: Device Characteristics and Spectral Properties of LEDs based on PF3/5am

[0060]   The PF3/5 polymer has the highest tendency to crystallize because of its highly symmetric and less bulky side-chains. The onset voltage for EL from devices with an PF3/5am6 emission layer is significantly lower compared to that of PF3/5 devices and the device brightness is higher as can be seen in Fig. 5. The EL spectrum of the non end-capped PF3/5 does not contain a red-shifted emission contribution but the colour stability is better for the end-capped PF3/5am6 - there is practically no change in the device emission after more than 15 min operation (PF3/5am6 = 0 min; pf3/5am6 opp = 15 min operation) as can be seen from the insert in Figure 5.
[0061]   In general, all of the devices comprising active layers of polyfluorenes end-capped with a charge-transporting moiety demonstrate stable colour characteristics.

Example 8: Alignment of PF2/6am

[0062]   Polyimide (PI) alignment layers were prepared by spin casting of a PI precursor at a total solid content of 30 g/L in the Merck-ZLI 2650 kit solvent at 2000 rpm for 50 s. After 15 min. softbaking at 80°C, the precursor was converted at 300°C for 1 hr. under rotary pump vacuum. PI layers were rubbed unidirectionally using a rubbing machine from E. H.C. Co., Ltd., Japan. The rotating cylinder was covered with a rayon cloth and rotated at 1400 rpm. The samples were passed twice under the cylinder at a translating speed of 2.2 mm/s. The depth of impression of the rubbing cloth onto the substrate was approximately 0.8 mm. Films of PF2/6am were spun of 10 g/1 toluene solution onto rubbed PI alignment layers. The final film thickness were 90 nm as measured with an Tencor α-step profiler. To induce monodomain alignment, films were annealed in an autoclave at a temperature of 145°C for two hours in a 0.1 bar Ar-atmosphere and cooled to room temperature at a rate of 5 K/min. As can be seen in Fig. 6 a dichroic ratio of 26 at 380 nm was obtained.

Example 9: Preparation of LEDs with aligned emission layer

[0063]   Polyimide precursor modified for hole transport was spin cast on ITO patterned glass substrates. Conversion, rubbing, spin coating of PF2/6am, and annealing were done as described in example 8. Ca/Al top electrodes were thermally evaporated. The overlap between the two electrodes resulted in device areas of 5 mm². The device characterization was carried out in an evacuated sample chamber.

Example 10: Device Characteristics and Spectral Properties of polarized LEDs

[0064]   The luminance-voltage curve of a typical polarized LED with an active layer of PF2/6am4 aligned on a hole transporting alignment layer is shown in Fig. 7. The device has an onset voltage for the polarized emission as low as 4.5 V, a brightness in excess of 200 Cd/m² at 10 V and a polarization ratio of the light emitted at 447 nm higher than 11 (see insert plot of Fig. 7).
[0065]   The features disclosed in the foregoing description and the claims may, both separately and in any combination thereof be material for realising the invention in diverse forms thereof.

Claims

1. A polyfluorene end-capped with at least one charge-transporting moiety.

2. A polyfluorene according to claim 1, wherein the charge-transporting moiety is selected from the group comprising electron-transporting moieties, hole-transporting moieties and ion-transporting moieties.

3. A polyfluorene according to any of claims 1 - 2, wherein the charge-transporting moiety is selected from the group comprising :
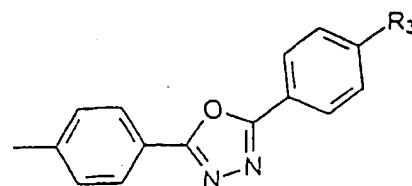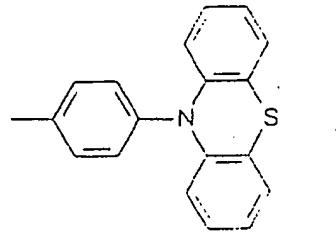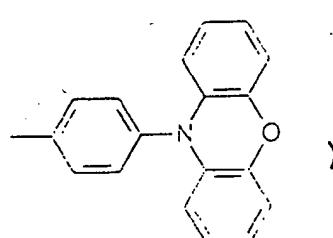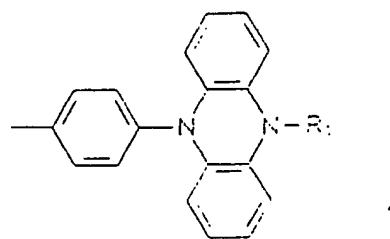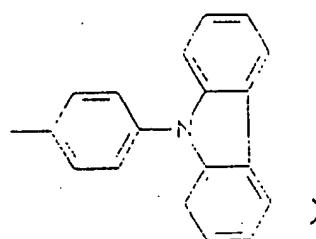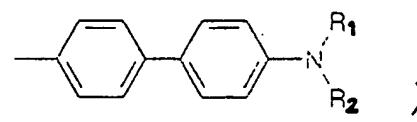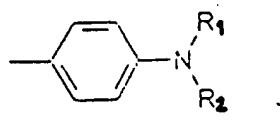
wherein R_1 and R_2 are independently at each occurrence selected from the group comprising straight chain C_{1-20} alkyl, branched C_{1-20} alkyl, aryl, substituted aryl, alkylaryl, substituted alkylaryl, alkoxyaryl, substituted alkoxyaryl, aryloxyaryl, substituted aryloxyaryl, dialkylaminoaryl, substituted dialkylaminoaryl, diarylaminoaryl and substituted diarylaminoaryl, and
wherein R_3 is independently at each occurrence selected from the group comprising straight chain C_{1-20} alkyl, branched C_{1-20} alkyl, aryl, substituted aryl, alkylaryl and substituted alkylaryl.

4. A polyfluorene according to claim 3, wherein R_1 and R_2 are independently at each occurrence selected from the group comprising 4-methylphenyl, 2-methylphenyl, phenyl, 1-naphthyl, 2-naphthyl, 4-methoxyphenyl, 2-methoxy-

phenyl, 4-dimethylaminophenyl, 2-dimethylaminophenyl, 4-diphenylaminophenyl and 4-phenoxyphenyl.

5. A polyfluorene end-capped with at least one moiety selected from the group comprising

wherein R_1 and R_2 are independently at each occurrence selected from the group comprising straight chain C_{1-20} alkyl, branched C_{1-20} alkyl, aryl, substituted aryl, alkylaryl, substituted alkylaryl, alkoxyaryl, substituted alkoxyaryl, aryloxyaryl, substituted aryloxyaryl, dialkylaminoaryl, substituted dialkylaminoaryl, diarylaminoaryl and substituted diarylaminoaryl, and
wherein R_3 is independently at each occurrence selected from the group comprising straight chain C_{1-20} alkyl, branched C_{1-20} alkyl, aryl. substituted aryl, alkylaryl and substituted alkylaryl.

6. A polyfluorene according to claim 5, wherein R_1 and R_2 are independently at each occurrence selected from the group comprising 4-methylphenyl, 2-methylphenyl, phenyl, 1-naphthyl, 2-naphthyl, 4-methoxyphenyl, 2-methoxyphenyl, 4-dimethylaminophenyl, 2-dimethylaminophenyl, 4-diphenylaminophenyl and 4-phenoxyphenyl.

7. A polyfluorene having the formula
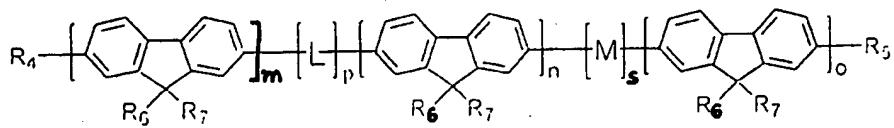
$$R_4 \left[\quad \right]_m \left[L \right]_p \left[\quad \right]_n \left[M \right]_s \left[\quad \right]_o R_5$$

wherein R_4 and R_5 are independently at each occurrence selected from the group comprising:

and H

R_1 and R_2 being independently selected from the group comprising straight chain C_{1-20} alkyl, branched C_{1-20} alkyl, aryl, substituted aryl, alkylaryl, substituted alkylaryl, alkoxyaryl, substituted alkoxyaryl, aryloxyaryl, substituted aryloxyaryl, dialkylaminoaryl, substituted dialkylaminoaryl, diarylaminoaryl and substituted diarylami-

noaryl,

R_3 being selected from the group comprising straight chain C_{1-20} alkyl, branched C_{1-20} alkyl, aryl, substituted aryl, alkylaryl and substituted alkylaryl,

and wherein R_6 and R_7 are independently at each occurrence selected from the group comprising straight chain C_{1-20} alkyl, branched chain C_{1-20} alkyl, aryl, substituted aryl, alkylaryl, substituted alkylaryl, $-(CH_2)_q-(O-CH_2-CH_2)_r-O-CH_3$,

q being selected from the range $1 \leq q \leq 10$, r being selected from the range $0 \leq r \leq 20$,

and wherein L and M are independently at each occurrence selected from the group comprising thiophene, substituted thiophene, phenyl, substituted phenyl, phenanthrene, substituted phenanthrene, anthracene, substituted anthracene, any aromatic monomer that can be synthesized as a dibromo-substituted monomer, benzothiadiazole, substituted benzothiadiazole, perylene and substituted perylene,

and wherein $m+n+o \geq 10$, each of m, n, o being independently selected from the range 1 - 1,000,

and wherein p is selected from the range 0 - 15,

and wherein s is selected from the range 0 - 15,

with the proviso that, if R_4 is H, R_5 is not H, and if R_5 is H, R_4 is not H.

8. A polyfluorene according to claim 7,
   wherein m, p, s, o are 0, and
   wherein R_4 - R_7 and R_1 - R_3 are as previously defined.

9. A polyfluorene according to any of the foregoing claims cross-linked to a polyfluorene according to any of the foregoing claims via at least one linkage selected from the group comprising a 9,9-spirobifluorene-linkage, a bifluorenyl-linkage, a bifluorenylidene-linkage and an α,ω-difluorenylalkane-linkage with a length of the alkane spacer in the range from 1 - 20 C-atoms.

10. A polyfluorene according to any of the foregoing claims which has at least one color-tuning moiety incorporated into the main chain.

11. A polyfluorene according to claim 10, wherein the color-tuning moiety is selected from the group comprising thiophene, substituted thiophene, phenyl, substituted phenyl, phenanthrene, substituted phenanthrene, anthracene, substituted anthracene, any aromatic monomer that can be synthesized as a dibromo-substituted monomer, benzothiadiazole, substituted benzothiodiazole, perylene and substituted perylene.

12. A polyfluorene according to any of the foregoing claims, which is liquid-crystalline.

13. A polyfluorene according to claim 12, which is liquid-crystalline at or above 70°C.

14. A polyfluorene according to any of claims 1 - 11, which is amorphous.

15. A polyfluorene selected from the group comprising

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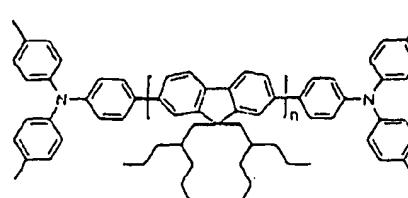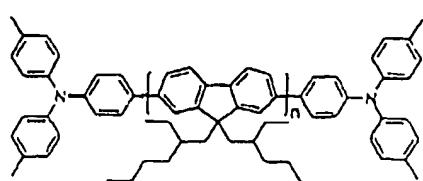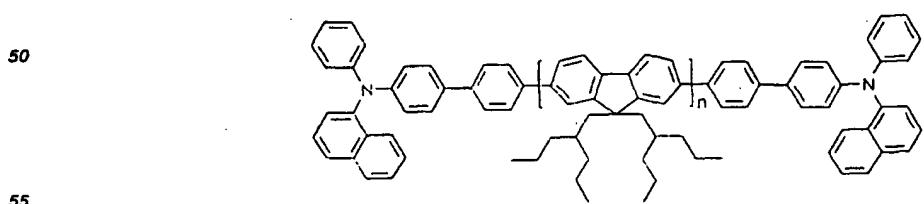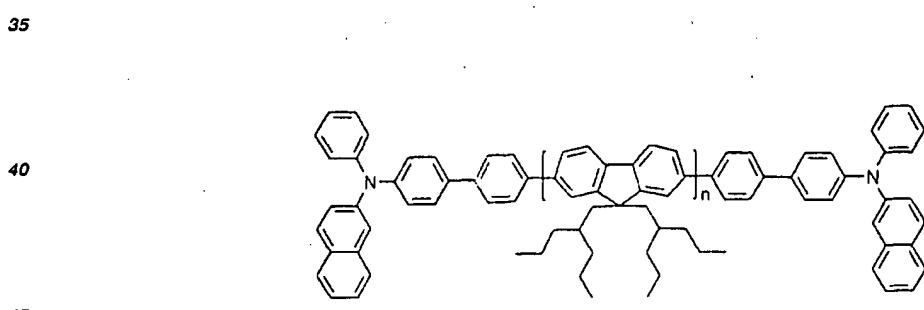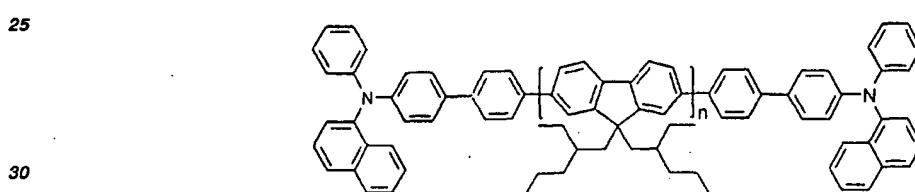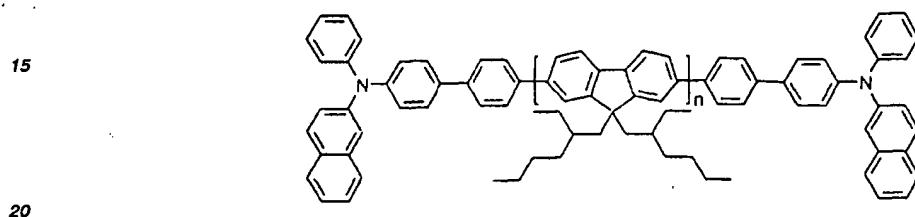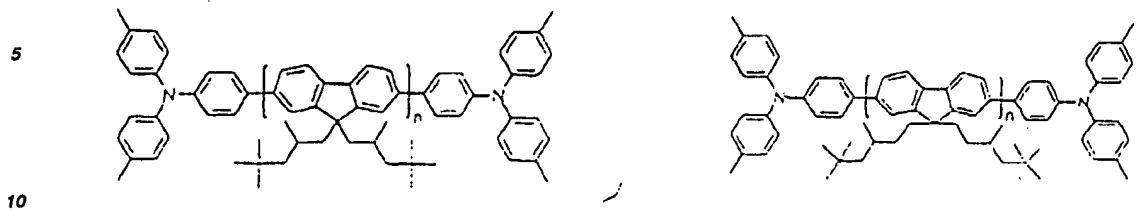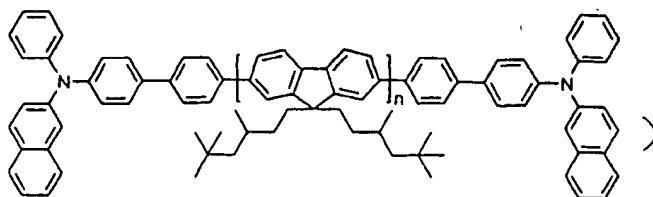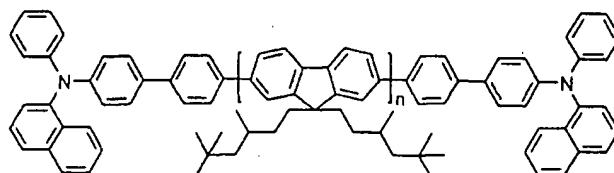
wherein n is as previously defined.

16. A film incorporating a polyfluorene according to any of the foregoing claims.

17. A film according to claim 16 which is aligned.

18. A film according to any of claims 16 - 17, incorporating at least one other substance.

19. A film according to claim 18, in which said other substance is selected from the group comprising fluorescent dyes, hole-transporting moieties, electron-transporting moieties. ion-transporting moieties, phosphorescent dyes, nanoparticles, low molecular weight liquid-crystalline moieties, other liquid-crystalline and/or fluorescent and/or phosphorescent and/or charge-transporting polymers.

20. A film according to any of the claims 16 - 19, deposited on an alignment layer.

21. A film according to any of the claims 16 - 20 having a thickness ranging from 10 nm to 2 μm.

22. A device selected from the group comprising FETs, photovoltaic elements, LEDs and sensors, incorporating a polyfluorene according to any of claims 1-15.

23. A device according to claim 22 incorporating another polymer.

24. A device according to claim 23 wherein said polymer is a luminescent polymer.

25. A device selected from the group comprising FETs, photovoltaic elements, LEDs and sensors, incorporating a film according to any of claims 16 - 21.

26. Use of a polyfluorene according to any of claims 1 - 15 in a film.

27. Use according to claim 24, wherein the film is an emission layer.

28. Use of a polyfluorene according to any of claims 1 - 15 in a device selected from the group comprising FETs, photovoltaic elements, LEDs and sensors.

29. Use of a film according to any of claims 16 - 21 in a device selected from the group comprising FETs, photovoltaic elements, LEDs, and sensors.

30. Use of a device according to any of claims 22 - 25 in combination with a liquid-crystal display (LCD).

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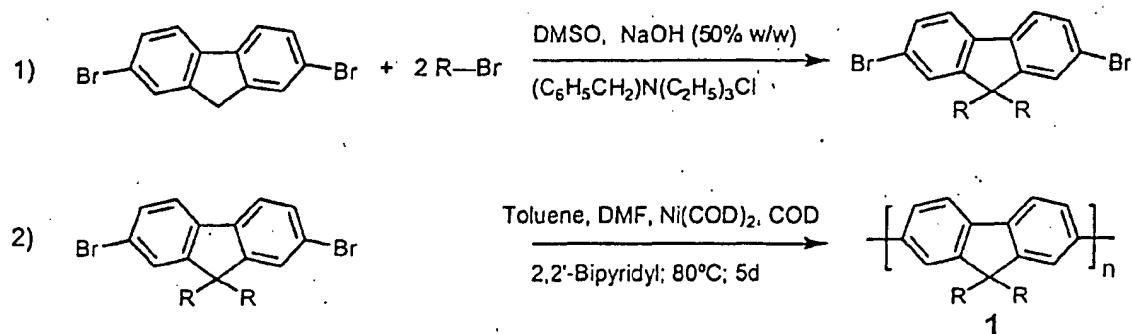
Fig. 1
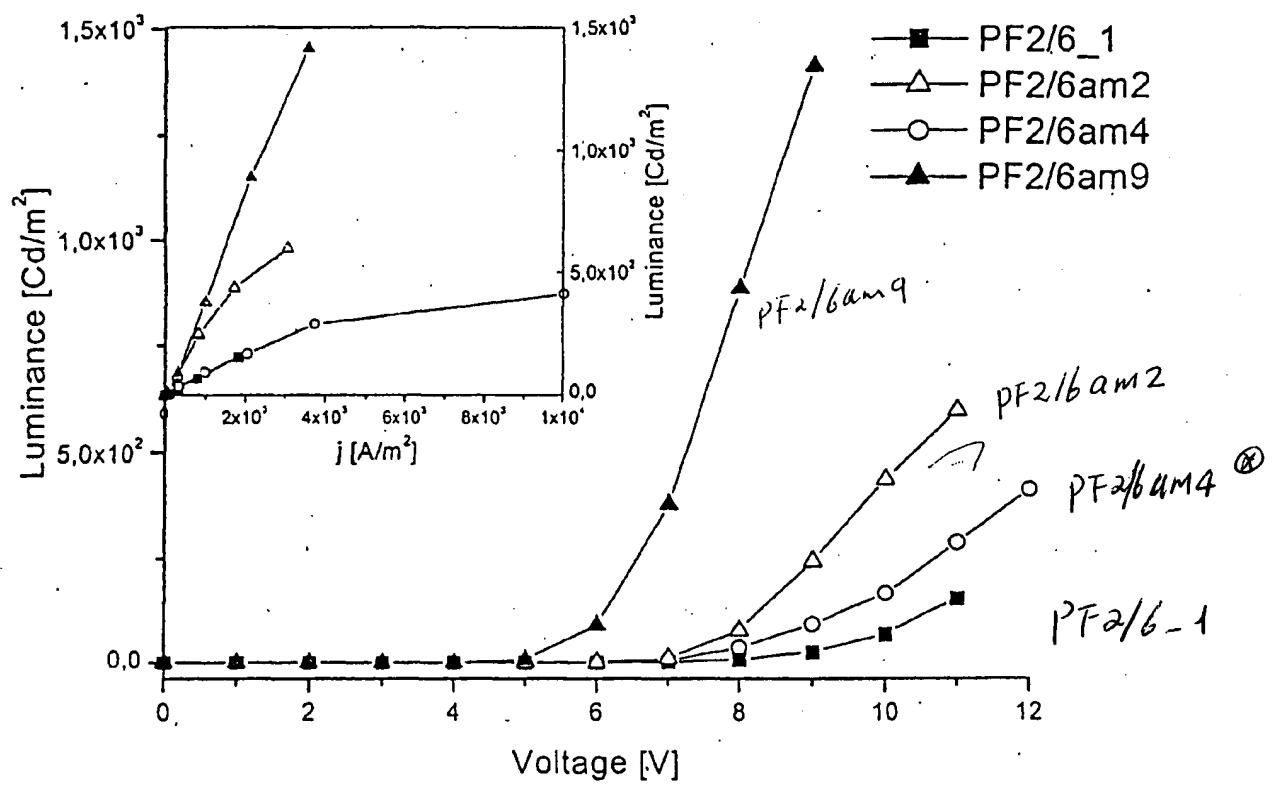
Fig. 2

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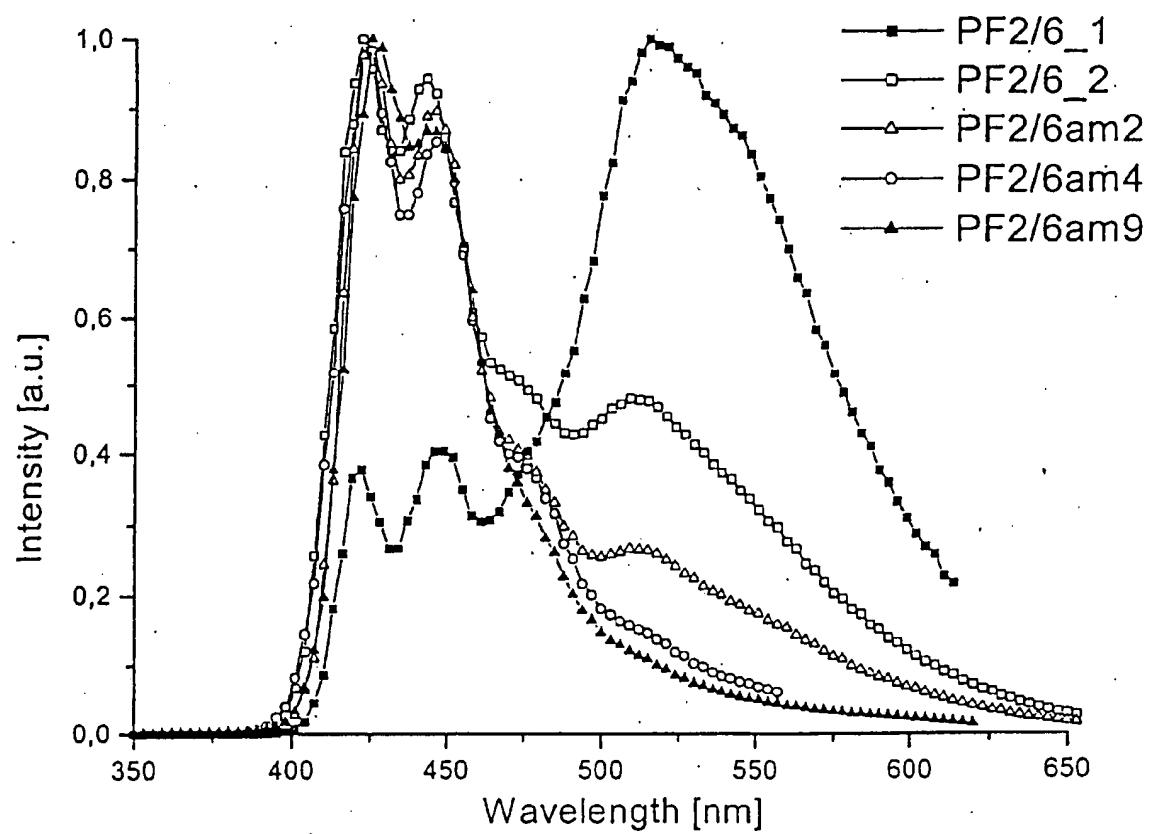
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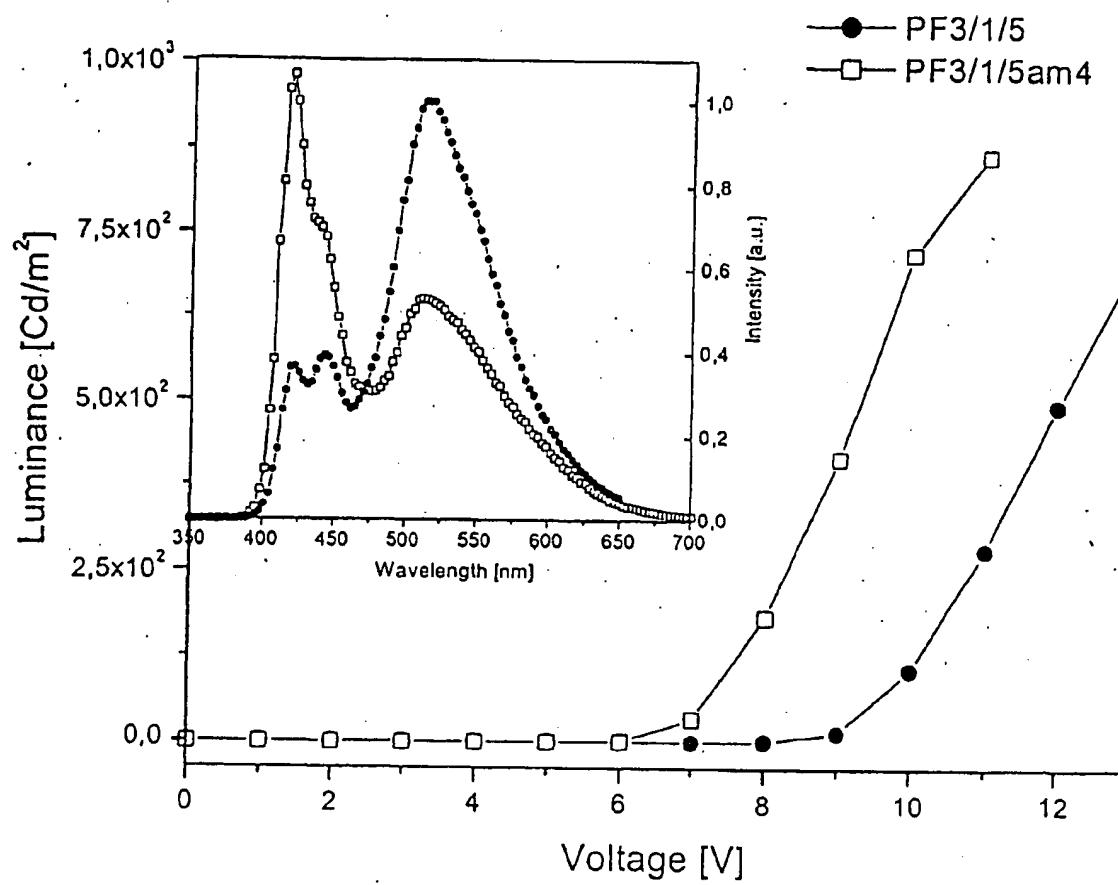
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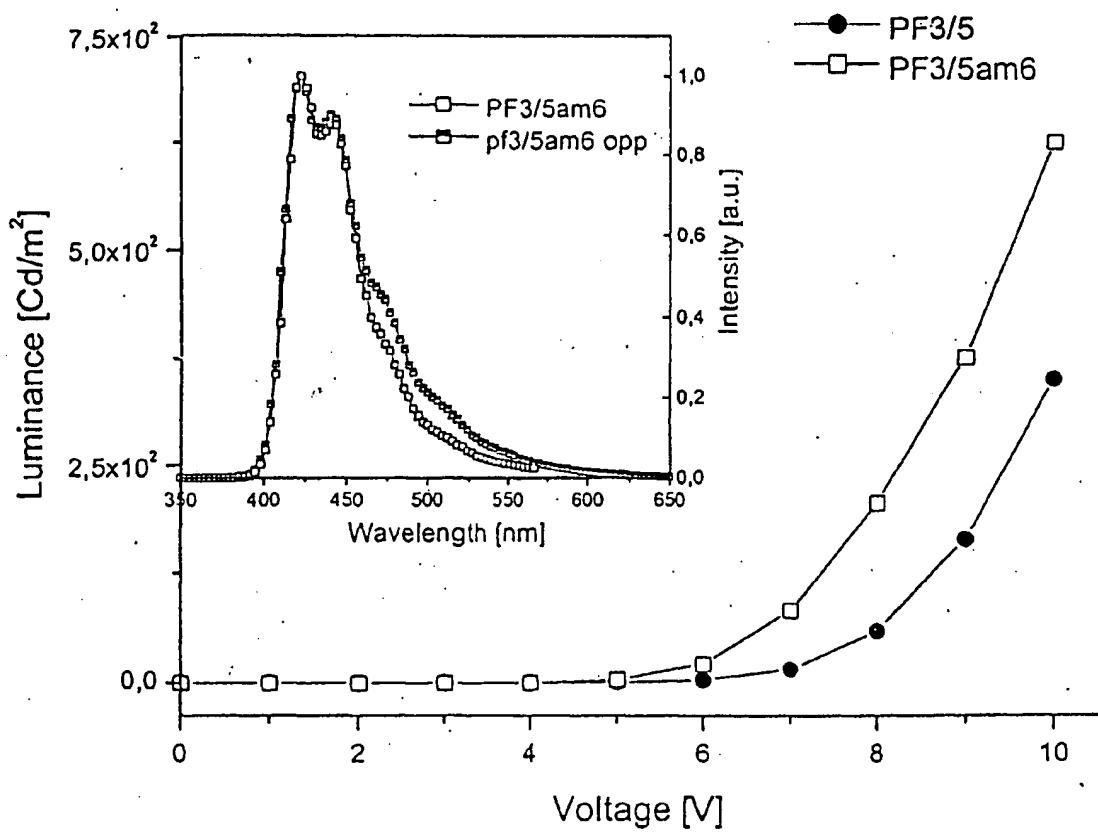
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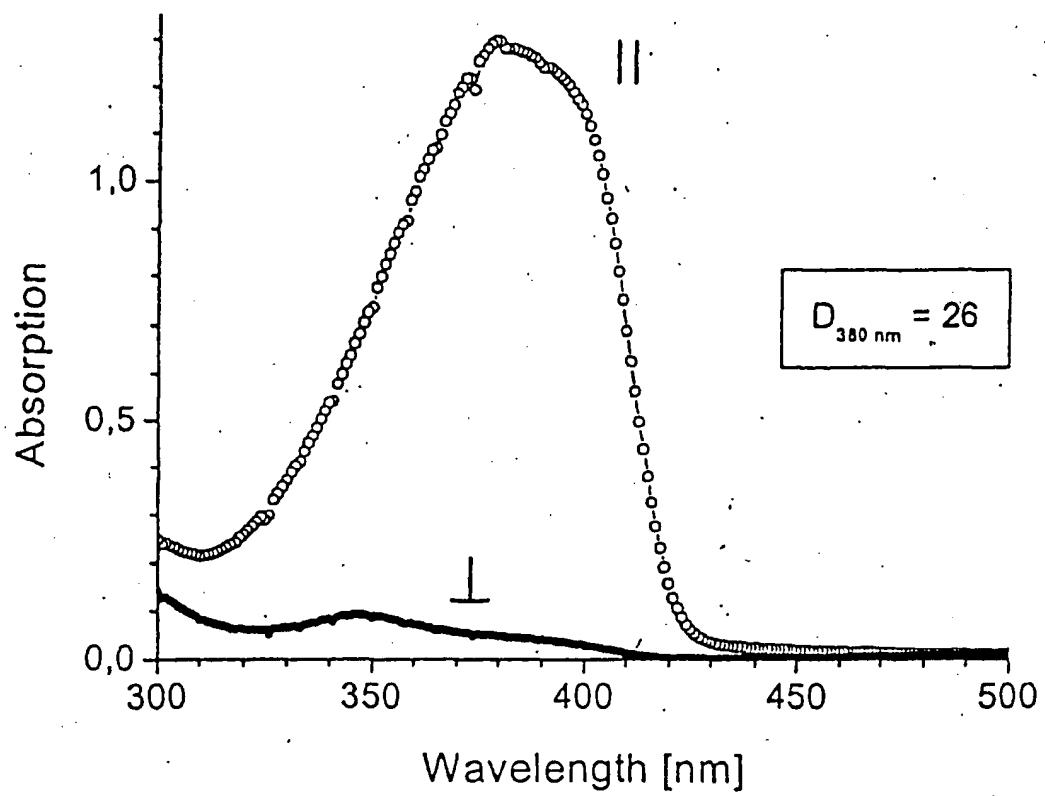
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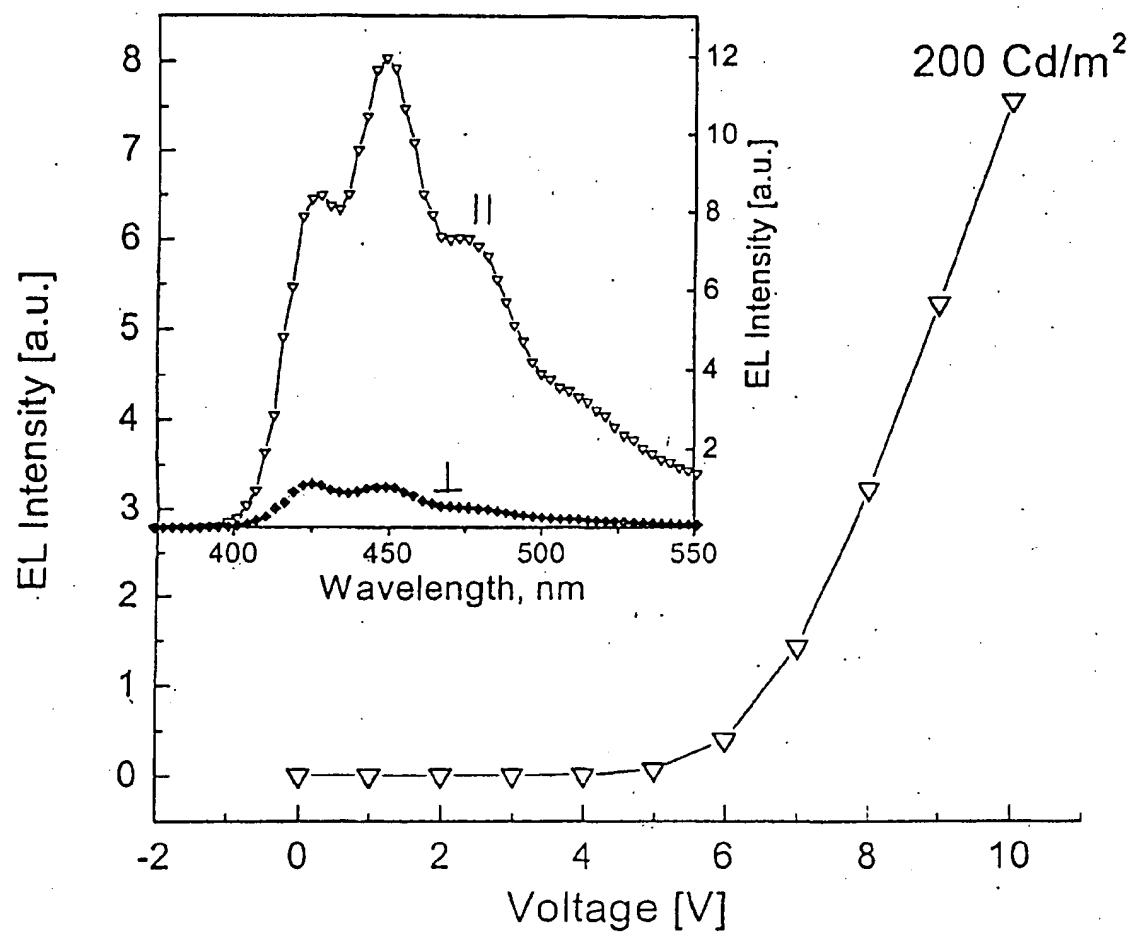
Fig. 7

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 00 10 8877

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	LEE J -I ET AL: "Light-emitting electrochemical cells based on poly(9,9-bis(3,6-dioxaheptyl)-fluorene-2,7-diyl)" 2ND INTERNATIONAL CONFERENCE ON ELECTROLUMINESCENCE OF MOLECULAR MATERIALS AND RELATED PHENOMENA, SHEFFIELD, UK, 15-18 MAY 1999, vol. 111-112, pages 195-197, XP000951433 Synthetic Metals, 1 June 2000, Elsevier, Switzerland ISSN: 0379-6779 * the whole document *	1,2,22, 24,26	C07C211/55 H01L51/30
A	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 02, 29 February 2000 (2000-02-29) & JP 11 322679 A (TOSOH CORP), 24 November 1999 (1999-11-24) * abstract *	1-4	
A	WO 99 54385 A (DOW CHEMICAL CO) 28 October 1999 (1999-10-28) * the whole document *	1-15, 22-30	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C07C H01L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	2 October 2000	Königstein, C

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

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WO 9954385	A	28-10-1999	CN	1263542 T	16-08-2000
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(54) Title: TRANSPARENT SUPPORT FOR ORGANIC LIGHT EMITTING DEVICE
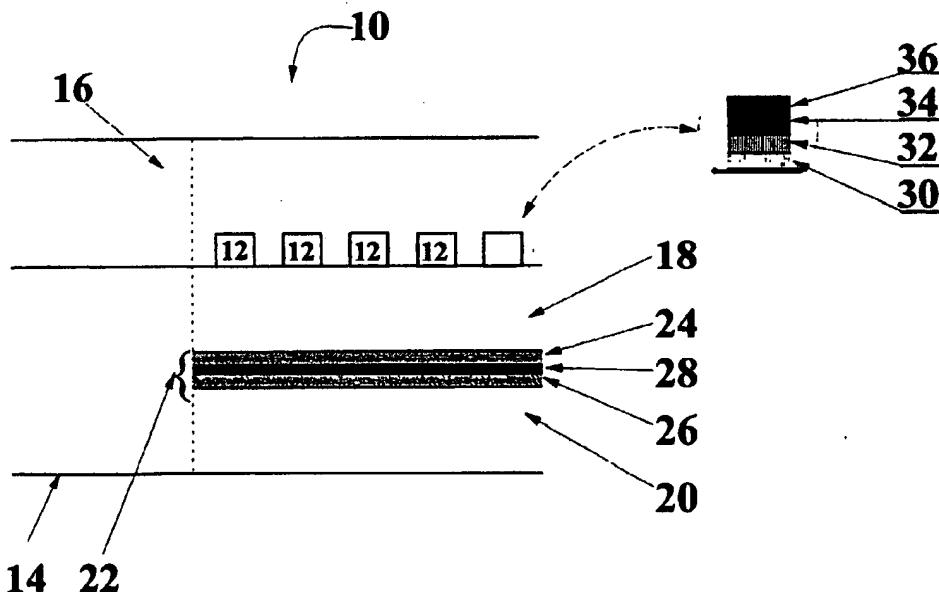
(57) Abstract: An improved transparent support substrate in an organic light emitting diode (OLED) device comprises an organic polymer support film and a composite layer on the support film which is disposed intermediate the support film and the diodes of the OLED; the composite layer has first and second discrete coating layers bonded together in opposed facing relationship; the layers are of material impermeable to oxygen and water vapor but contain inadvertent discontinuities which result in discontinuity-controlled permeation of oxygen and water vapor.

GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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TRANSPARENT SUPPORT FOR ORGANIC LIGHT EMITTING DEVICE

TECHNICAL FIELD

This invention relates to organic light emitting diode (OLED) devices and
methods for their production; the invention is more especially concerned with
oxygen and water vapor impermeable flexible substrates for such devices and
methods of producing such flexible substrates.

BACKGROUND ART

An organic light emitting diode (OLED) device is an emissive display in which a
transparent substrate is coated with a transparent conducting material, for
example, indium-tin oxide (ITO) which forms a hole-injecting electrode as the
lowest layer of a light emitting diode. The remaining layers of the diode
commencing with the layer adjacent the ITO layer comprise a hole transporting
layer (HTL), an electron transporting layer (ETL) and an electron-injecting
electrode.

The hole-transporting layer is essentially a p-type semi-conductor and the
electron-transporting layer is essentially an n-type semi-conductor. These are
organic layers and in particular are conjugated organics or conjugated polymers,
the latter are poor conductors without dopants but are doped to conduct holes (p-
type) or electrons (n-type).

The electron-injecting electrode is typically a metal such as calcium,
lithium or magnesium.

When a voltage is applied to the diode, electrons flow towards the hole-
transporting layer and holes flow towards the electron-transporting layer. This
produces electron-hole recombinations which release energy as light. Collectively
the hole-transporting layer (HTL) and the electron transporting layer (ELT) form
the electroluminescent layer (EL) of the diode.

Such OLEDs provide a new generation of active organic displays of high
efficiency, large view angle, excellent color definition and contrast,

and most important of low cost. In those displays, high-quality images are created by a matrix of the light emitting diodes encapsulated in transparent materials.

The diodes are patterned to form a pixel matrix, where a single-pixel
5   junction or EL emits light of a given color . All organic displays, designed so far, contain oxygen- and moisture-sensitive components, namely organic semiconductors and electron-injecting metals.

.   Consequently, the diodes require protection by means of an impermeable layer forming a barrier to oxygen and water vapor, which
10   impermeable layer envelops the layers of the diode, and a substrate supporting the enveloped diode, of high transparency, and which is impermeable providing a barrier to oxygen and water vapor.

Thus far glass plate has been the supporting substrate of choice, since it has excellent barrier and transparency properties. On the other
15   hand, glass plate has the drawbacks of brittleness, high-weight, and rigidity.

A strong demand exists for plastic-film substrate material that may bring flexibility, high impact resistance, low weight, and, most of all, which may enable roll-to-roll processing, as opposed to batch processing which has been used thus far. Such plastic film substrate material should,
20   of course, be essentially impermeable, displaying low oxygen and water vapor transmission rates.

Although one may expect some further improvement in oxygen and moisture resistance of organic semiconductors employed in the diodes, extremely water-sensitive electron-injecting metals such as Ca, Li and Mg
25   seem to be irreplaceable until a major breakthrough is made in solid state physics or in display design, both rather unlikely in the predictable future.

Other properties, which the substrate material for organic displays should present, such as thermal resistance, low roughness, and low costs

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the 42nd Annual Technical Conference, Boston 1999, p. 496]. Organic photovoltaic devices also require similar, flexible, barrier materials, so do liquid crystal flexible displays, where barrier requirements are, however, less demanding.

5   Organic displays are proposed for such equipment as high-resolution computer displays, television screens, cell-phones and advanced telecommunication devices etc., which require μm-scale precision manufacturing, vacuum operations and lithography. In other words: technologies similar to those at present used in microelectronics. Other

10   applications include large scale displays for advertising and entertainment, and various communication devices. These latter applications may require lower precision in manufacturing, processing in inert-dry atmospheres, roll-to-roll operations, inexpensive methods of patterning, for example, stamping or ink jet printing. In other words: low-cost technologies, perhaps

15   similar to those at present used in special quality graphic-printing.

The problem is thus to develop flexible polymer films as supporting substrates which are essentially barriers to oxygen and water vapor and which can be produced at low thickness sufficient for their support functions and such that they can be readily employed in commercial

20   manufacture of the organic devices in roll-to-roll processing.

In order to satisfy market requirements relative to existing competitive organic displays having glass plate substrates or the more conventional inorganic light emitting devices, a polymer film substrate for an OLED would need to prevent oxygen and water molecules from

25   reaching the diode components for a period of years and typically for a life of at least 10,000 hours.

It is known in the flexible packaging art, to coat polymer films or

water vapor. In practice it is impossible in commercial manufacture to produce such coatings without some pinholes or other defects which permit passage of oxygen and water molecules through the otherwise impermeable coating. This may not be a serious problem in the flexible packaging art

5   where the packaging is typically protecting a food product of limited shelf life. However, the levels of permeability that may be acceptable in the short working life of flexible packaging in the food and other industries will certainly not meet the more exacting requirements for organic displays based on organic light emitting diodes which must have a life of years

10   rather than the days or weeks which represent the typical useful or working life of flexible packaging.

DISCLOSURE OF THE INVENTION

This this invention seeks to provide an organic light emitting diode

15   device having a flexible film substrate of enhanced impermeability to oxygen and water vapor.

This invention also seeks to provide such a device in which the flexible film substrate comprises an organic polymer film having an impermeable barrier coating thereon and in which loss of impermeability

20   arising from pinholes and other types of defects in the coating is reduced.

Still further, this invention seeks to provide a flexible film barrier support substrate for an OLED device.

This invention also seeks to provide a method of producing a flexible film barrier support substrate for an OLED device.

25   Still further, this invention seeks to provide a method of producing an OLED device having a flexible film barrier support substrate.

Still further, this invention seeks to provide an OLED device in

one of the substrate and the covering being of enhanced impermeability to oxygen and water vapor.

In accordance with one aspect of the invention there is provided in an organic light emitting diode device, in which light emitting organic 5 diodes are encased in a barrier envelope comprising a transparent substrate supporting said diodes and a barrier covering, said substrate and covering being impermeable to oxygen and water vapor, the improvement wherein at least one of said substrate and said covering comprises: i) an organic polymer support film, and ii) a composite layer on said support film and 10 disposed intermediate said support film and said light emitting diodes, said composite layer comprising first and second discrete coating layers bonded together in opposed facing relationship, each of said first and second coating layers being impermeable to oxygen and water vapor when formed as a continuous coating, each of said first and second coating layers having 15 inadvertent discontinuities therein such that said coating layers exhibit discontinuity-controlled permeation of oxygen and water vapor therethrough.

In accordance with another aspect of the invention there is provided in a method of manufacturing an organic light emitting device in which 20 light emitting diodes are formed on a transparent substrate impermeable to oxygen and water vapor, the improvement wherein the transparent substrate is as defined hereinbefore.

In accordance with still another aspect of the invention there is provided a transparent support substrate for an organic light emitting diode 25 device comprising: i) an organic polymer support film, and ii) a composite layer on said support film, said composite layer being adapted to be disposed between said support film and light emitting organic diodes of an

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relationship, each of said first and second coating layers being impermeable to oxygen and water vapor when formed as a continuous coating, each of said first and second coating layers having inadvertent discontinuities therein such that said coating layers exhibit discontinuity-controlled

5 permeation of oxygen and water vapor therethrough.

In accordance with yet another aspect of the invention there is provided a method of producing a transparent support substrate for an organic light emitting device comprising: a) coating a first transparent organic polymer film surface with a first coating layer, b) coating a second

10 transparent organic polymer film surface with a second coating layer, c) bonding said coating layers together in opposed facing relationship to form a composite layer between said first and second polymer film surfaces, each of said first and second coating layers being impermeable to oxygen and water vapor when formed as a continuous coating; each of said first and

15 second coating layers having inadvertent discontinuities therein such that said coating layers exhibit discontinuity-controlled permeation of oxygen and water vapor therethrough.

DESCRIPTION OF PREFERRED EMBODIMENTS

20 i)   OLED

Organic light emitting diode devices rely on electroluminesce, their general structure is well established and is not the subject of this invention. Such devices employy component layers which are sensitive to oxygen and water molecules and must thus be effectively sealed from ingress of oxygen

25 and water vapor while maintaining transparency to light and different desired physical characteristics.

In general an OLED comprises a plurality of light emitting diodes mounted on a support substrate. The support substrate must have high

diodes placed on the support substrate are covered by a barriercovering, also impermeable to oxygen and water vapor. The support substrate and covering together form a barrier envelope encasing the diodes.

ii)   Substrate

5   The supporting substrate of the invention comprises an organic polymer support film having a composite layer thereon. The composite layer comprises a pair of coatings bonded together in opposed. facing relationship.

The substrate may comprise a polymer film with the composite layer

10   thereon or it may comprise a pair of polymer films in opposed facing relationship with the composite layer sandwiched therebetween such as to form an intermediate layer between the polymer films.

The substrate may suitably have a thickness of 5μm to 10 mm, more typically 25μm to 1000 μm.

15   a)   Polymer Films

The support film should be transparent and of any suitable organic polymer, including homopolymers, copolymers and terpolymers which can be fabricated as a suitably thin film having the necessary and desirable physical characteristics to form a barrier support substrate for the diodes,

20   physical characteristics of particular importance are strength and flexibility at desired film thickness for the OLED device.

While the polymer films do not need to be and generally will not be impermeable to oxygen and water vapor, polymer films which are of lesser permeability to oxygen and water vapor will generally be preferred to those

25   of higher permeability.

Suitable polymers for the polymer film include, by way of example, polyolefins, for example, polyethylene and polypropylene;

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polyesters;   polyarylates,   polyacrylates,   polyethyleneterephthalate;
polyethylenenaphthalate;   polystyrene;   polyamides;   polyimides;
polyethersulfone, and polyorganosilicones, as well as other transparent
polymers and copolymers including other high T_g polymers. The polymer

5   film may include one or more layered polymer components.

Preferred polymer films are chosen from high T_g polymers, for
example cyclopolyolefins, polyethersulfones, polyarylates, and from
polyethyleneterephthalate and polyethylenenaphthalate.

The polymer films will have a thickness to achieve the desired
10   substrate thickness.

Where the support substrate comprises a pair of polymer films with
the coating layers therebetween, the polymer films may be of the same or
different polymers.

b)   Impermeable Composite

15   The composite layer provides a barrier to oxygen and water vapor
and is composed of a pair of discrete coating layers which when formed as
continuous coatings are impermeable to oxygen and water vapor.

On the other hand, since discontinuities are inevitable in the discrete
coating layers, each coating layer will exhibit discontinuity-controlled
20   permeation of oxygen and water molecules therethrough.

As it will be described below, each discrete coating layer may be
formed as a single coating or may be composed of a plurality of single
coatings preferably of different materials, which also show the presence of
inadvertent discontinuities. The plurality of single coatings are each formed
25   as discrete coatings of the coating layer.

These inadvertent discontinuities described more fully below are
essentially pinholes which form during deposition of the coating layer and
are inherent in the coating techniques available, and other types of defects

which arise from external factors during or subsequent to deposition of the coating layers.

The coating layers may be the same or different; by way of example, suitable coating layers may be formed from transparent materials such as

5   oxides, nitrides, mixed compositions, and salts; for example, SiO_x, SiO_xC_y, Si_xN_y, $Si_xN_yC_z$, SiO_xN_y, TiO_x, Al_xO_y, SnO_y, indium-tin oxide, magnesium fluoride, magnesium oxyfluoride, calcium fluoride, tantalum oxide, yttrium oxide, zirconium oxide, barium oxide, magnesium oxide,   and mixtures thereof, wherein x is from 1 to 3, y is 0.01 to 5 and z is 0.01 to 5. Particular

10   examples include silica, alumina and titania; other examples include amorphous carbon, borosilicate, sodium and potassium glass.

Preferred coating layers are stoichiometric or non-stoichiometric silicon dioxide deposited by plasma, stoichiometric or non-stoichiometric silicon nitride deposited by plasma; and multilayer structures including

15   discrete coatings of one or both of silicon dioxide and silicon nitride, and polymer coatings, for example polyacrylates or organic plasma polymers obtained from organosilicones, hydrocarbons or acrylates.

Each coating layer suitably has a thickness of 10   nm to 10μm, preferably 60 nm to 5μm and more preferably 100 nm to 2μm.

20   In a particular embodiment, one or both coating layers may be composed of a plurality of single coatings, for example alternate inorganic- and organic coatings; in such case, the coatings of the plurality are formed as discrete coatings in separate coating operations, and there are at least two such discrete coatings in a coating layer, such as those described in the

25   literature []. This is most desirable especially in the case of coating layers thicker than 150-200 nm, where single coatings of different materials provide necessary mechanical stability and barrier properties.

The barrier substrate must be transparent to light and suitably will have a transparency greater than 65% and preferably greater than 85%, measured according to ASTM D 1746-97.

Each coating layer which forms a barrier to oxygen and water vapor

5 should suitably display an oxygen transmission rater lower then 1 $cm^3/(m^2day\cdot atm)$, and preferably lower than 0.01 $cm^3/(m^2day\cdot atm)$ and more preferably lower than 0.005 $cm^3/(m^2day\cdot atm)$ measured according to ASTM F 1927 or D 3958; and a water vapor transmission rate (WVTR) lower than 0.01 $g/(m^2day\cdot atm)$, preferably lower than 0.005 $g/(m^2day\cdot atm)$

10 and more preferably lower than 0.001 $g/(m^2day\cdot atm)$ as measured according to ASTM F 1249.

c)   Adhesives

The pair of coating layers are suitably bonded or laminated together with an adhesive.

15   In one embodiment of the method of producing coating layers, each layer is independently formed as a discrete (single or multiple layer) coating on a film substrate to form a pair of coated film substrates which are then bonded together, coating layer to coating layer. In this way the coating layers form a composite layer sandwiched between a pair of film substrates.

20   In a first embodiment this assembly forms the support substrate.

In a second embodiment one of the film substrates is composed of first and second polymer films having release properties at the interface ·therebetween for ready removal of the first polymer film from the substrate after the bonding of the two film substrates in coating layer to coating layer

25 contact.   In this way the coating layers form a composite layer on the second polymer film as the support substrate, and the first polymer film functions as a thin temporary protective film on the side of the support

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The release coating may be formed from the same classes of adhesive employed for bonding the coating layers together, but with appropriate adjustment, as well known in the adhesive art, to introduce the required release characteristics.

5   Adhesives that may be employed for bonding the coating layers and for the release coating include thermoplastic-and elasto-plastic polymers; polymers which are curable by radiation, for example, ultraviolet or electron-beam; heat, by chemical initiators or by combinations thereof; organic or organic-containing adhesives, such organics being, for example,

10   acrylics, urethanes, epoxides, polyolefins, organosilicones and others; composite ceramic materials, composite organic/ceramic materials; and products of plasma-polymerization, oligomerization, or curing of organic-, organosilicon and other organometallic compounds, either volatile or deposited by other means such as spraying, casting or dip-coating.

15   Particular examples of adhesives include elastomer based adhesives, for example; synthetic organic adhesives, for example, phenolic resins, acrylic resins, polyvinyl acetals, epoxies, polyamides or silicone adhesives; and inorganic polymer adhesives, for example, soluble silicates such as may be prepared by fusion of silica and alkali metal carbonates.

20   The adhesive forms an adhesive layer bonding the two coating layers. The adhesive layer may suitably have a thickness of 50 nm to 10 μm, preferably 100 nm to 2μm. Especially advantageously the adhesive layer has a thickness less than the dimensions of thediscontinuities.

In preferred embodiments the adhesive exhibits a scavenging effect

25   towards oxygen, water or both and such scavenging may be, for example, by adsorption, absorption or chemical reaction. In this way the adhesive layer provides an additional barrier.

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The method of producing the support substrate essentially involves coating each of a pair of organic polymer films, as described hereinbefore, with a coating layer, as described hereinbefore.

It will be understood that the pair of films may be derived from a single sheet or roll of film, with the coated film being cut to provide two separate coated films. However, in a continuous or continual manufacture, the coating layers will preferably be formed independently on separate films.

The coating layers may be applied by various coating techniques, but preferably by physical vapor deposition (PVD), for example, evaporation or sputtering or by chemical vapor deposition (CVD), for example, plasma enhanced chemical vapor deposition (PECVD) or organic vapor phase deposition (OVPD). These methods are capable of producing very thin coatings, which are stable and flexible but of satisfactory hardness, and which exhibit low oxygen and water vapor permeations. PVD and PECVD are carried out under vacuum. In this way a pair of film substrates is obtained each having a coating layer.

The substrates are then bonded to, or adhered, together coating layer to coating layer, thereby forming a supporting substrate which comprises the pair of film substrates in opposed facing relationship with the coating layers forming a composite layer sandwiched between the film substrates.

In another embodiment the second of the pair of film substrates is itself a composite substrate comprising a pair of film layers bonded together with an adhesive whereby the film layers can be readily separated. After bonding the coating layers together the outermost of the film layers of the second film substrate provides a temporary protective layer which is removed when the diodes are to be mounted on the support substrate. In this case the diodes are supported in contact with the remaining film layer

v)   Applications of Support Substrate

In one embodiment the support substrate forms the front, transparent support of an OLED device, the diodes of the device being encapsulated on the other side by a suitable non-transparentbarrier covering, also impermeable to oxygen and water vapor, thus providing the OLED device having one-side light emission. A suitable nontransparent barrier covering material may be of a metal can, plate, foil or an evaporated film, as is well known in the OLED art.

In another embodiment the support substrate forms the front, transparent background of an OLED device, and the barrier covering on the other side is also formed of a transparent support substrate of the invention, thus providing an OLED device that is transparent and emits light on both sides. A support substrate according to the invention thus encapsulates the diodes both as the front support and as the rear barrier covering, together forming a barrier envelope.

In still another embodiment, the support substrate of the invention forms the barrier covering and the front support of the OLED device is of another material, for example glass, as known in the OLED art.

The support substrate according to the invention may be used also in other types of devices, such as liquid crystal displays or in organic photovoltaic devices, which are known in prior art to require transparent materials impermeable to oxygen and water vapor.

vi)   Manufacture of OLED

The OLED is suitably formed under vacuum conditions to minimize introduction of contaminants which may chemically or physically damage the OLED or alter its characteristics. Small molecule diode components, sensitive to oxygen and water molecules, are deposited onto the support

example, be deposited onto the support substrate for example from a solution in a suitable organic solvent in an inert atmosphere.The support substrate is produced as outlined hereinbefore. Thereafter, in a vacuum process a transparent conductive layer, for example, indium-tin oxide, is

5   deposited on the support substrate.

The transparent conductive layer is patterned to form the lower electrode of the diode, which is the hole-injecting layer. On the hole-injecting layer there is deposited, successively, the hole-transporting layer and the electron-transporting layer, both of which are organic layers, and

10   thereafter the electron-injecting layer which forms the upper electrode, and which may be, for example, of calcium, lithium, magnesium or aluminium, or suitable metal alloys.

The afore-mentioned layers may be deposited by vacuum evaporation, well known in the OLED art.

15   Instead of vacuum evaporation, the organic layers and the upper electrode may also be deposited by printing, for example ink jet printing, stamping or other transfer techniques in an inert atmosphere, as well known in the PLED art.

20   **BRIEF DESCRIPTION OF DRAWINGS**

FIG. 1 illustrates schematically a portion of an OLED of the invention in a first embodiment;

FIG. 2 illustrates schematically a portion of an OLED of the invention in a second embodiment;

25   FIG. 3 illustrates schematically the OLED of FIG. 1 partly exploded;

FIG. 4 illustrates schematically the low permeation in a support substrate of the invention;

FIG. 5 demonstrates graphically the calculated permeation through the support substrate of FIG. 4 relative to horizontal distance between defect centres;

FIG. 6 illustrates schematically a support substrate of the invention;

FIG. 7 is a plot demonstrating the probability (PR) of matching random defects face-to-face vs defect number density (DN) in the coating layers of a support substrate of the invention; and

FIG. 8 is a schematic representation of a system for producing the support substrate of the invention.

DESCRIPTION OF PREFERRED EMBODIMENTS
WITH REFERENCE TO DRAWINGS

With further reference to FIG. 1, there is illustrated a portion of an OLED 10 having a plurality of diodes 12 on a support substrate 14 and an impermeable envelope 16.

Support substrate 14 comprises polymer films 18 and 20 with a composite layer 22 therebetween.

Composite layer 22 comprises a coating layer 24 formed on polymer film 18 and a coating layer 26 formed on polymer film 20. Coating layers 24 and 26 are bonded together by an adhesive layer 28.

FIG. 1 includes an exploded view of a diode 12. Each diode 12 is of the same form. Diode 12 comprises, in a stack, a hole-injecting layer 30, a hole-transporting layer 32, an electron-transporting layer 34 and an electron-injecting layer 36.

In the manufacture, coating layer 24 is first formed as a discrete layer on polymer film 18 and separately coating layer 26 is formed as a discrete layer on polymer film 20.

With reference to FIG. 2, there is shown an OLED 200 which differs

The manufacture of support substrate 214 is essentially the same as that for support substrate 14 except that polymer film 18 comprises a pair of support films 38 and 42 (film 42 is not shown) which are bonded together in opposed facing relationship by a release coating (not shown). Prior to

5 assembly of OLED 200, support film 42 is removed to expose support film 38 for contact with the diodes 12.

With further reference to FIG. 3, there is shown an OLED of FIG. 1, partly exploded so that the arrangement of diodes in the OLED 10 can be observed.

10 With further reference to FIGS. 4 and 6, there is further illustrated composite layer 22 of the OLED 10 of FIGS. 1 and 3.

Coating layer 24 has inadvertent defects 50 and 52 and coating layer 26 has inadvertent defects 54, 56 and 58, which defects are of essentially the same size as the thickness of adhesive layer 28. Since such inadvertent

15 defects are random and thus not necessarily aligned in the opposed coating layers 24 and 26, a tortuous path for passage of oxygen and water vapor is provided as illustrated by the arrows. In this way a diminished defect controlled permeation is exhibited.

In FIG. 6 the composite layer 22 is shown in conjunction with the

20 polymer films 18 and 20 in the support substrate 14.

With further reference to FIG. 8, there is illustrated schematically a system for manufacture of the support substrate 14 of FIG. 6. The system comprises an assembly 60 having a roll 62 of polymer film 18 and a roll 64 of polymer film 20.

25 Assembly 60 further includes degassing roll 66, a coating drum 68 for polymer film 18 and a coating drum 70 for polymer film 20 and an adhesive deposition zone 72.

Assembly 60 further includes laminator 74, a rewind roll 76 and a

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In operation polymer films 18 and 20 are continuously fed from rolls 62 and 64 respectively over degassing rolls 66 to coating drums 68 and 70 respectively.

An adhesive layer 25 is applied to coating layer 24 on one face of
5   polymer film 18 in adhesive deposition zone 72 and adhesive layer 25' is applied to coating layer 26 on one face of polymer film 20 in adhesive deposition zone 72, in such a way that coating layers 24 and 26, applied to the faces of polymer films 18 and 20, are in facing relationship.

The thus coated polymer films 18 and 20 are fed through laminator
10 74 where lamination occurs with coating layers 24 and 26 in opposed facing relationship. Lamination involves application of an adhesive between the coating layers 24 and 26 and cure of the adhesive, the nature of which depends on the adhesive employed.

The resulting laminate which is support substrate 14 is fed onto
15 rewind roll 76.

The support substrate 14 may be fed directly to a station for OLED manufacture or may be stored and subsequently transported to a station for OLED manufacture.

The manufacture is suitably carried out under vacuum which
20 minimizes the risk of defects in coating layers 24 and 26 as a result of dust particles or other contaminants. After deposition, the coating layers 24 and 26, which are the working impermeable layers providing a barrier to oxygen and water vapor, are shielded or protected by the polymer films 18 and 20.

25 Experimental and Explanations
    Discontinuities
    a)   Nature of Defects.

The coating layers in the composite layer of the barrier support substrate each contain inadvertent discontinuities which permit permeation of oxygen and water vapor through the otherwise impermeable layers.

5   The decrease in permeation of oxygen and water vapor through a polymer film substrate resulting from inorganic, impermeable coatings is usually characterized by a Barrier Improvement Factor (BIF), namely the measured ratio of permeation of the bare substrate to that of the coated film. Such inorganic coatings may decrease permeation of oxygen and water vapor through polymer films by several orders of magnitude, thus showing

10   a BIF of 10^3, 10^4 or more for thin polymer film substrates. However, the barrier properties of simple coated polymer films are still at least two orders of magnitude higher than those required for an OLED.

The permeation of gases through silica-coated plastic films is a discontinuity or defect-controlled phenomenon [A. S. da Silva Sobrinho,

15   G. Czeremuszkin, M. Latrèche, G. Dennler and M. R. Wertheimer, Surf. and Coat. Technol. 116-119, 1204 (1999), H. Chatham, Surf. Coat. Technol. 78, 1 (1996)]. This means that the residual permeation is due to the presence of micrometer- and submicrometer-size defects in the coatings. Size and shape of defects, their number density, and thickness of the plastic

20   substrate film, are found to be important parameters that determine permeation through coated films.

Three main types of inadvertent defects in the coatings may be distinguished, namely:

- submicrometer-size pinholes, characteristic to the method of deposition

25   and related to surface micro-roughness of the polymer film,

- sub-micrometer to multimicrometer-size defects due to dust and micro-particles,

cracks and scratches created during production, handling and converting

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All of those defects are practically inevitable in real industrial-scale (roll-to-roll) manufacture operations.

Evenly distributed, sub-micrometer-size pinholes contribute to overall permeation, and lead to a quasi one-dimensional diffusion front at

5 the back face of the coated film. Permeation through those small pinholes decreases the lifetime of an organic display, causing its uniform deterioration. On the other hand, large defects, for example, related to dust particles, will form zones of localized diffusion, where the rapid local deterioration of the device will be observed as "dark spots" in the display.

10 The presence of a single, dust-related defect in the barrier encapsulation may cause failure of the display much before its expected lifetime, thus justifying the rejection of the final product by quality control. Therefore, technology which provides barrier-coated films, practically free of large defects, will be of very high value to the organic display industry.

15 Decreasing the number density of defects in inorganic barrier-coated films produced by physical vapor deposition (PVD) and plasma enhanced chemical vapor deposition (PECVD) is a very difficult task, since some requirements are in mutual contradiction. For example, the required very low permeability (low defect density) calls for thick inorganic barrier

20 coatings [A. S. da Silva Sobrinho, G. Czeremuszkin, M. Latrèche, and M. R. Wertheimer, J. Vac. Sci. Technol. A 18, 149 (2000).], but these thick barrier coatings are usually brittle, and show high internal stresses, low flexibility and low stretchability. Polymer films, even of optical grade, show certain surface micro-roughness, which, as described above, is an

25 important source of submicron-size pinholes in the coatings deposited on such films.

b) Defect-Controlled Permeation

In order to characterize sub-micrometer size defects in transparent

technique based on plasma etching has been developed. Defects are thereby rendered visible in optical microscopy (OM), their patterns may be observed by simple visual inspection, and their number densities and size distributions can be evaluated with relative ease. In addition a simple model

5 of permeation through defects in otherwise impermeable coatings has been developed, which allows a better understanding and analysis of the mechanism of permeation through barrier-coated polymer films [G. Czeremuszkin, M. Latrèche, A. S. da Silva Sobrinho, and M. R. Wertheimer, SVC, Proc 42nd Annual Tech. Conf., 176 (1999).]. Using this

10 model, it has now been determined that only a very thin surface layer of the polymer film substrate, in the immediate vicinity of the barrier-coating, plays a significant role in the overall barrier performance. This has permitted an evaluation of the maximum BIF for a pair of discrete coating layers bonded together on a polymer film, displaying defect-controlled

15 permeation and devoid of large pinholes, cracks or scratches, which is merely twice that of the same polymer film with a single coating layer. The upper-limit of applicability of the model, corresponding to BIF =1, expected for very thick substrate films was identified. It was found that the lower-limit of the applicability of derived equations corresponds to a

20 substrate polymer film with a thickness close to the size of typical defects in the coating. Below this lower-limit thickness value, the model cannot be used.

A special technique for detection of micrometer-size defects in transparent barrier coatings deposited on transparent polymer films has

25 been developed. The technique is based on plasma etching, and renders defects and their patterns visible in optical microscopy (OM) and detectable by simple visual inspection. A simple model of permeation through defects

For purposes of this invention the model of permeation was modified by adopting the theory of heat transport in thin plates, for diffusion of permeant through thin films. As the conclusion from theoretical considerations, the invention deposits a barrier coating onto each of two

5   independent polymer films and bringing them together, coated face to coated face in permanent contact, for example by laminating, using a layer of adhesive, preferably having low permeation to water vapor and oxygen. Four critical parameters that determine permeation through the proposed structure have been identified:

10   A. Size of defects in the component barrier-coatings;

B. Number density of defects in the coatings;

C. Thickness of the adhesive layer, which should preferably be lower than the size of defects.

D. The material of the adhesive layer, which should preferably show

15   low permeability to the permeants.

As confirmed by experimental results, the overall permeation through transparent barrier-coated polymer films is lowered, according to the present invention, by at least an additional two orders of magnitude or

20   more. For large defects in a single coating, for example, those due to dust particles, this translates to an extremely low or negligible probability of finding a "dark spot" in a large organic display having a barrier support substrate of the invention.

The invention thus relies on previously unforeseen observations and

25   conclusions from a novel approach to very thin, double coated layers on polymer film support substrates in which the coating layers have micrometer and sub-micrometer-size defects. In order to calculate the

transport and the transport of permeant through thin plates are described by the same types of diffusion equations).

On this basis the permeation P through a pair of coating layers of a composite layer of the invention can be defined by:

5

$$P = \frac{2\pi D \, \Phi \circ L}{\operatorname{acosh}\left(\dfrac{d^2}{2R_0^2 - 1}\right)} \qquad (I)$$

where each coating layer contains randomly distributed defects of the same
10   circular shape and the same diameter $2R_0$.

Typically, $2R_0 = 0.5 - 2\mu m$ for micrometer-size pinholes, and $2R_0 = 10\ \mu m$ for dust-related defects, where the number density of those defects may reach several thousands per cm^2, and not more than a few per cm^2, respectively.

15   This situation is equivalent to permeation through the layer with a defect controlled permeation. The plastic film of small thickness, L, and of diffusion coefficient of the permeant, D, has the coatings on both sides, which contain the defects of radius R_0. Those defects, in both coatings, are separated by a horizontal (projected) distance d. The film is then exposed
20   to the permeant only from one side, concentration of which at the surface zones on both sides is then Φ_0 and 0, respectively.

This is equivalent to permeation through a transparent substrate of the invention comprising a pair of transparent polymer films having the composite layer therebetween, with a defect-controlled permeation. It is
25   assumed that the polymer films are of thickness L, and of diffusion

R_0, and the defects in both coatings are separated by an overall horizontal distance d. The transparent substrate is then exposed to the permeant only from one side, concentration of which at the surface zone or both sides is then Φ_0 and O, respectively.

5   FIG. 4 presents schematically the situation when the thickness of composite layer 22 is comparable with the average size of defects 50, 52, 54, 56 and 58 in the coating layers 24 and 26. As explained below, permeation of gases through such a structure may be very low, and BIF $>>$ 2 may be expected. This is due to the tortuous path of permeant molecules,

10   which will encounter a much longer effective path of diffusion in the bulk of the composite layer, when transported from one defect 50 in the coating layer 24 to an adjacent defect 54 in the coating layer 26.

In particular, defects 50 and 52 in coating layer 24 and defects 54, 56 and 58 in coating layer 26 occur randomly so that on a statistical probability

15   basis defects 50 and 52 are remote from, and in non-opposed relationship with defects 54, 56 and 58.

FIG. 5 shows the calculated permeation through a support substrate of the invention in which the coating layers contain a single (circular) defect of radius Ro each, vs. the horizontal (projected) distanced between

20   centers of those defects.

In the case of $d<R_0$, the defects partly overlap, and the permeation may only be 2x lower than the permeation through a single coating. In the case of $d>>R_0$, permeation decreases rapidly, which, however, strongly depends on the thickness of the polymer film. It can be seen from FIG. 5

25   that permeation can be two orders of magnitude lower than permeation through a polymer film having a single coating layer. This may be achieved when the polymer film is very thin, and when the polymer material possesses low permeability of the permeant in question

The principle of this invention may be further explained by reference to FIG. 6. FIG. 6 shows a support substrate 14 of the invention comprising polymer films 18 and 20 each having been previously coated with transparent coating layers 24 and 26 respectively, each containing random

5   defects 50, 52 and 54, 56 and 58, respectively, and then brought together in permanent contact by means of adhesive lamination with adhesive layer 28. Overall permeation through this support substrate 14 film will be much lower than permeation through each distinct coated film (film 18 with coating layer 24 or film 20 with coating layer 26). The support substrate 14,

10   according to the invention, may exhibit super-barrier properties (OTR < 0.001 cm^3/(m^2day·atm), and WVTR < 0.000001 g/(m^2day·atm), even if both component films show much poorer barrier performance. More important, however, the substrate 14 according to the invention practically eliminates harmful effects of permeation through large defects in the coating layers,

15   such as those created by dust particles.

FIG. 7 presents in two cases (a and b) the probability of matching random defects face-to-face in two coating layers brought together in accordance with the invention. A simplified statistical analysis used here, based on so-called Bernoulli trials, leads to overestimation of the

20   probability. In the analysis, the circular "defect" of a given radius (representing a pinhole in the second coating layer) is randomly placed on the surface representing the first coating layer, which contains a given number of identical, circular defects. The probability of defects overlapping is then calculated. The procedure is repeated, so that the total number of

25   trials corresponds to the number of defects in the second coating layer. Obviously, in the Bernoulli Scheme, the defect may be randomly placed in the position already occupied by another defect (and previously taken in the

trials), which gives rise to the source of the overestimation. Therefore the real probability of defects matching is even lower than the one calculated.

As can be seen from the presented analysis, and this is confirmed by experimental results, the overall permeation through transparent barrier-
5   coated plastic films may be lowered, in accordance with this invention, by an additional two orders of magnitude with probability exceeding 99.9%. In the case of large defects, such as those due to dust particles, the number density of which is not high in the original coating layers, this translates into an extremely low or negligible probability of finding a "dark spot" in a
10 large organic display produced using the support substrate according to the invention.

EXAMPLES

Polymer films of polyethyleneterephthalate and polypropylene were
15 "cleaned" of large dust particles by blowing compressed nitrogen over their surfaces. A controlled number of sodium chloride micro-crystals were deposited onto the surface of the polymer films using an aerosol of salt solution in water, created ultrasonically. The deliberately contaminated films were then coated with 36 or 70 nm of silica using the PECVD
20 method, from HMDSO/O_2/Ar precursor mixture. The films were then washed with flowing water (DI/RO, 18 MΩ), which dissolved the micro-crystals, and were then dried with dry nitrogen. Since the polymer films were not silica coated in places previously occupied by the crystals, the above procedure provided numerous well-characterized defects in the
25 coating. The sodium chloride crystals deposited onto the polymer films, and corresponding defects in the coating, were clearly visualized, the latter using the defect detection technique described above. In order to control the

number of defects and to avoid false dust-related pinholes, the

coated films were laminated face-to-face using a thin layer of an UV-curable adhesive, which shows lower oxygen permeation than adhesives typically used in bonding of polymer films. Lamination was performed both in a vacuum and in air. Up to two orders of magnitude improvement of the

5   barrier (vs. single-side coated film with defects) was observed.

In another experiment, two typical silica-coated polymer films were laminated using a ~3 μm thickness of soft adhesive, of similar permeation to those typically used in bonding of plastic films. The measured OTR value was only ~2x lower than the one determined for the single component

10   film.

The results obtained in this experiment part are summarized in Table I.

The experiments confirm the theoretical findings, and they show that:

15   - the thickness of the adhesive, more precisely, the distance between the two coating layers containing defects, should be preferably smaller than the size of the defects in the coatings;

- the material of an adhesive between the two coating layers should preferably display low permeability to the permeant.

20   In accordance with the invention it has been determined that there are four parameters that particularly determine permeation through the support substrate of the invention.

A. The size of defects in the component transparent barrier-coating layers, which are responsible for permeation through such

25   component barriers;

B. The number density of defects in the component transparent barrier-coating layers, which determines permeation through

_____ _ _ _____ ___ ___t L___:___.

27

C. The distance between the coating layers of the two component transparent barrier-coatings containing defects (equivalent to the thickness of the laminating or adhesive layer), which, according to the invention, should preferably be less than the typical size of defects mentioned in A above.

5

D. The material(s) filling the gap between the two coating layers (equivalent to the material of an adhesive layer), which, according to this invention, should preferably show low permeability to the permeant.

10   Support substrates prepared according to the invention show substantial improvement in barrier properties. When the parameters shown in A-D above are properly chosen, this improvement may reach or exceed two orders of magnitude.

Advantages of the support substrates of the invention, are the

15   following:

- practically total elimination of permeation through large-scale, dust-related defects, thus preventing "dark spot" appearance in organic displays;

- significant improvement of barrier properties, thus allowing one to

20   reach the super-barrier level with coatings, which themselves do not show sufficiently low permeation;

- excellent flexibility of the film in handling and converting, due to the position of the coatings close to the neutral plane for bending;

- protection of the coating layers against mechanical damage, as a

25   result of their being sandwiched between polymer films.

CLAIMS

1.   In an organic light emitting device in which light emitting diodes are encased in a barrier envelope comprising a transparent substrate supporting
5   said diodes and a barrier covering, said substrate and covering being impermeable to oxygen and water vapor, the improvement wherein at least one of said substrate and said covering comprises:

i)   an organic polymer film, and

ii)   a composite layer on said film and disposed intermediate said film
10   and said light emitting diodes,

said composite layer comprising first and second discrete coating layers bonded together in opposed facing relationship, each of said first and second coating layers being impermeable to oxygen and water vapor when formed as a continuous coating, each of said first and second coating layers
15   having inadvertent discontinuities therein such that said coating layers exhibit discontinuity-controlled permeation of oxygen and water vapor therethrough.

2.   A device according to claim 1 wherein both said substrate and said
20   covering are formed from said film and said composite layer.

3.   A device according to claim 1 wherein said substrate is formed of said film and said composite layer.

25   4.   A device according to claim 1, 2 or 3, wherein at least one of said discrete coating layers is composed of a plurality of discrete single coatings of different materials.

5.   A device according to claim 1, 2, 3 or 4, wherein said transparent substrate has a transparency greater than 65%, by ASTM D 1746-97.

6.   A device according to claim 5, wherein said transparency is greater than 85%.

7.   A device according to claim 1, 2, 3, 4, 5 or 6 , wherein said transparent substrate comprises first and second organic polymer support films in opposed facing relationship with said composite layer sandwiched therebetween.

8.   A device according to claim 1, 2, 3, 4 5, 6 or 7, wherein said composite layer has an oxygen transmission rate by ASTM F1927 and D3985 lower than 0.1 $cm^3/(m^2day\cdot atm)$.

9.   A device according to claim 8, wherein said oxygen transmission rate is lower than 0.005 $cm^3/(m^2day\cdot atm)$.

10.   A device according to any one of claims 1 to 9, wherein said composite layer has a water vapor transmission rate lower than 0.01 $g/(m^2day)$ by ASTM F1249.

11.   A device according to claim 10, wherein said water vapor transmission rate is lower than 0.005 $g/(m^2day)$.

12.   A device according to any one of claims 1 to 11, wherein said transparent substrate has a thickness of 5μm to 10 mm and said first and second coating layers each have a thickness of 100 nm to 2 μm.

13. A device according to any one of claims 1 to 12, wherein said first and second coating layers are bonded together with an adhesive layer such that said coating layers are spaced apart by a distance preferably less than

5   the dimensions of the inadvertent discontinuities in said coating layer.

14. A device according to any one of claims 1 to 12, wherein said first and second coating layers are bonded together with an adhesive layer preferably displaying low permeability to oxygen and water vapor.

10

15. A device according to claim 1 wherein said covering is formed of said film and said composite layer.

16. In a method of manufacturing an organic light emitting device in

15   which light emitting organic diodes are formed on a transparent substrate impermeable to oxygen and water vapor, the improvement wherein the transparent substrate comprises:

i)   an organic polymer support film, and

ii)   a composite layer on said support film and disposed intermediate

20   said support film and said light emitting diodes,

said composite layer comprising first and second discrete coating layers bonded together in opposed facing relationship, each of said first and second coating layers being impermeable to oxygen and water vapor when formed as a continuous coating, each of said first and second coating layers

25   having inadvertent discontinuities therein such that said coating layers exhibit discontinuity-controlled permeation of oxygen and water vapor therethrough.

17.   A method according to claim 16 wherein each of said discrete coating layers is a single coating.

18. A method according to claim 16 where at least one of said first and 5 second discrete coating layers is composed of a plurality of discrete single coatings of different materials.

19.   A transparent support substrate for an organic light emitting device comprising:

10   i)   an organic polymer support film, and

ii)   a composite layer on said support film, said composite layer being adapted to be disposed between said support film and light emitting organic diodes of an organic light emitting device, said composite layer comprising first and second discrete coating layers bonded together in opposed facing 15   relationship, each of said first and second coating layers being impermeable to oxygen and water vapor when formed as a continuous coating, each of said first and second coating layers having inadvertent discontinuities therein such that said coating layers exhibit   discontinuity-controlled permeation of oxygen and water vapor therethrough.

20

20.   A method according to claim 19 wherein each of said discrete coating layers is a single coating.

21.   A method according to claim 19 where at least one of said first and 25   second discrete coating layers is composed of a plurality of discrete single coatings of different materials.

22.   A substrate according to claim19, 20 or 21, having a transparency greater than 65%, by ASTM D1746-97.

23.   A substrate according to claim 22, wherein said transparency is greater than 85%.

5   24.   A substrate according to claim 19, 20, 21, 22 or 23, wherein said transparent substrate comprises first and second organic polymer support films in opposed facing relationship with said composite layer sandwiched therebetween.

10   25.   A substrate according to claim 19, 20, 21, 22, 23 or 24, wherein said composite layer has an oxygen transmission rate by ASTM F1927 and D3985 lower than 0.1 $cm^3/(m^2 day \cdot atm)$.

26.   A substrate according to claim 25, wherein said oxygen transmission
15   rate is lower than 0.005 $cm^3/(m^2 day \cdot atm)$.

27.   A substrate according to any one of claims 19 to 26, wherein said composite layer has a water vapor transmission rate lower than 0.01 $g/(m^2 day)$ by ASTM F1249.

20
28.   A substrate according to any one of claims 19 to 27, wherein said transparent substrate has a thickness of 5 μm to 10 mm and said first and second coating layers each have a thickness of 100 nm to 2μm.

25   29.   A substrate according to any one of claims 19 to 28, wherein said first and second coating layers are bonded together with an adhesive layer such that said coating layers are spaced apart by a distance preferably less than the dimensions of the inadvertent discontinuities in said coating layers.

30.   A substrate according to any one of claims19 to 28, wherein said first and second coating layers are bonded together with an adhesive layer preferably displaying low permeability to oxygen and water vapor.

31.   A substrate according to claim 30, wherein said inadvertent discontinuities in said first and second coatings occur randomly such that on a statistical probability basis discontinuities in said first coating layer are remote from, and in non-opposed relationship, with discontinuities in said second coating layer.

32.   A method of producing a transparent support substrate for an organic light emitting device comprising:

a)   coating a first transparent organic polymer film surface with a first coating layer;   .

b)   coating a second transparent organic polymer film surface with a second coating layer;

c)   bonding said coating layers together in opposed facing relationship to form a composite layer between said first and second polymer film surfaces,

each of said first and second coating layers being impermeable to oxygen and water vapor when formed as a continuous coating; each of said first and second coating layers having inadvertent discontinuities therein such that said composite layer exhibits discontinuity-controlled permeation of oxygen and water vapor therethrough.

33.   A method according to claim 32 wherein each of said discrete coating layers is a single coating.

34.   A method according to claim 32 where at least one of said first and second discrete coating layers is composed of a plurality of discrete single coatings of different materials.

5   35.   A method according to claim 33, wherein said transparent support substrate   has an oxygen transmission rate by ASTM F1927 and D3985 lower than 0.005 $cm^3/(m^2day \cdot atm)$.; and wherein said composite layer has a water vapor transmission rate lower than 0.01 $g/(m^2day)$ by ASTM F1249.

10   36.   A method according to claim32 or 35, wherein said transparent substrate has a thickness of 5 µm to 10 mm and said first and second coating layers each have a thickness of 100 nm to 2µm; and wherein said first and second coating layers are bonded together with an adhesive layer impermeable to oxygen and water vapor.

15

37.   A method according to claim 32, wherein said first polymer film surface is defined in a first polymer film, and said first polymer film comprises first and second support films bonded in opposed facing relationship with a release adhesive layer, and step a) comprises coating a

20   surface of said second support film with said first coating layer, and including a final step of:

     e)   separating said first support film from said second support film.
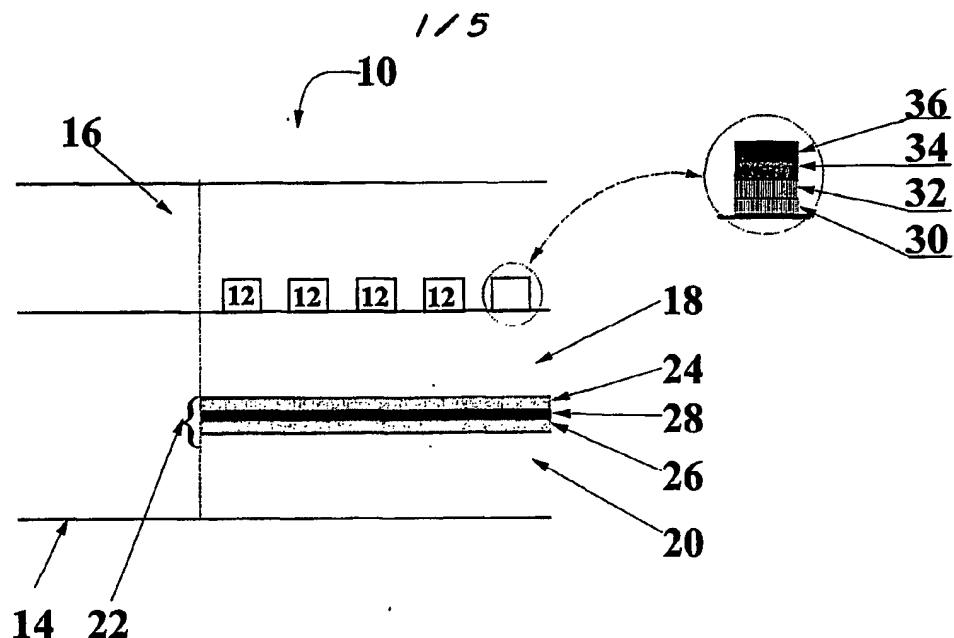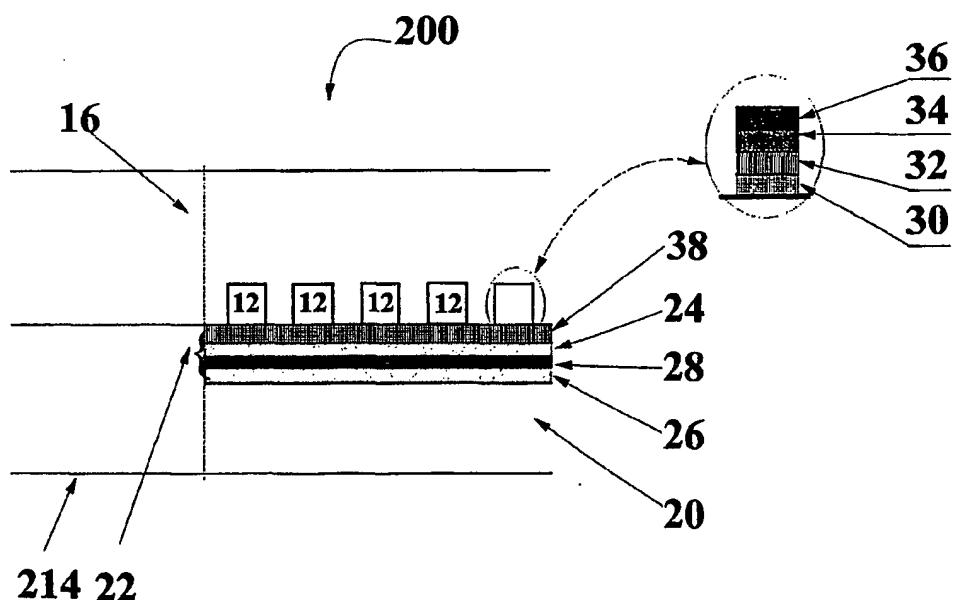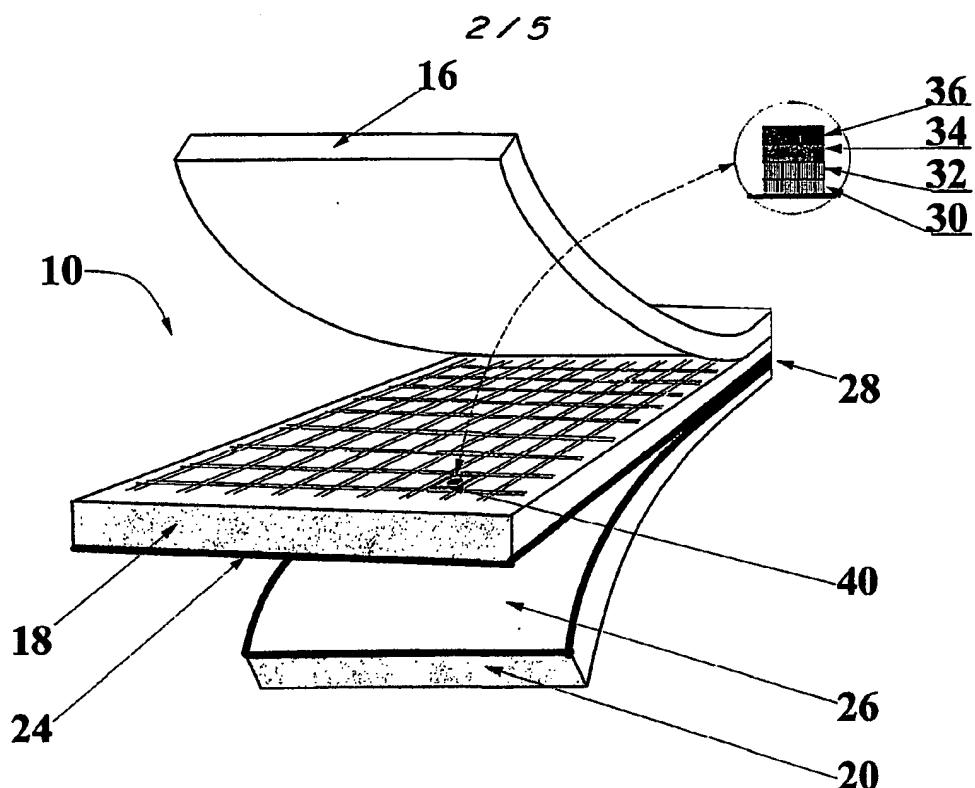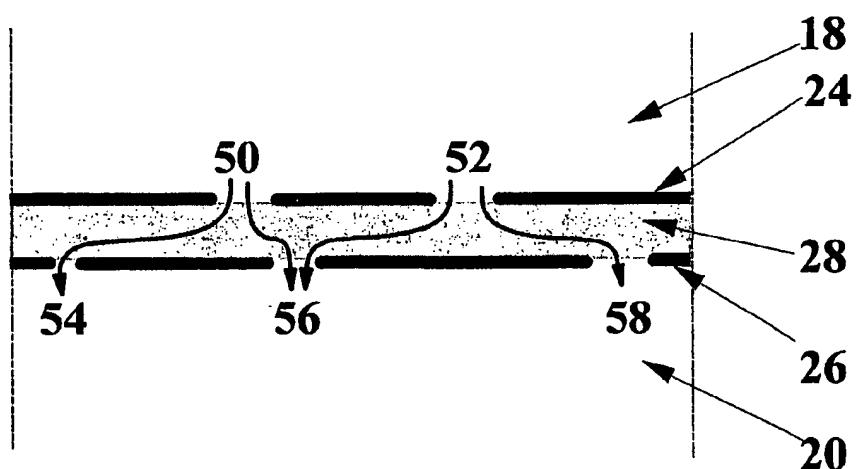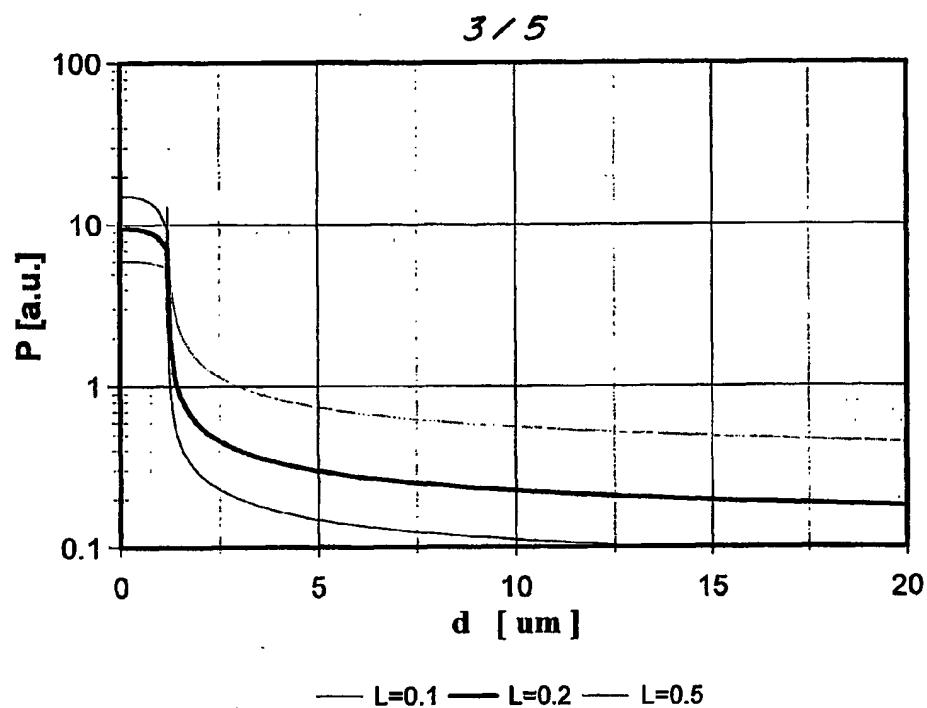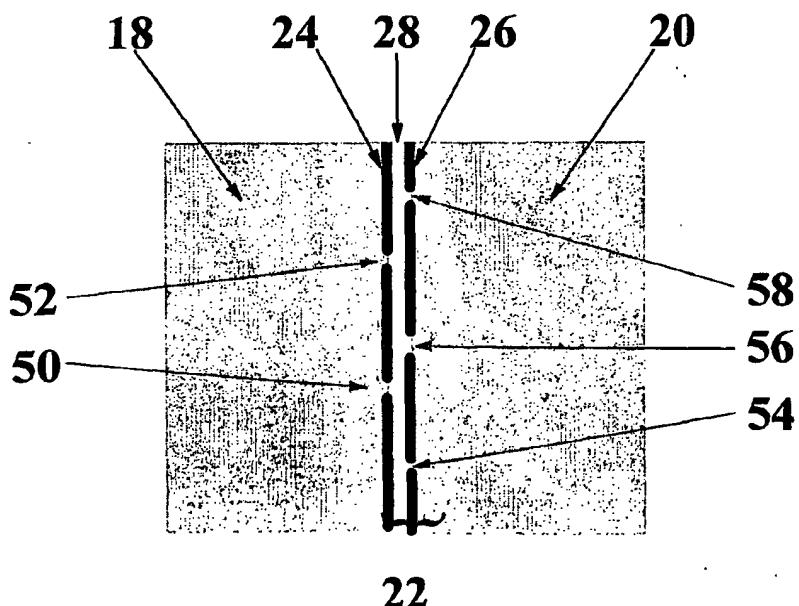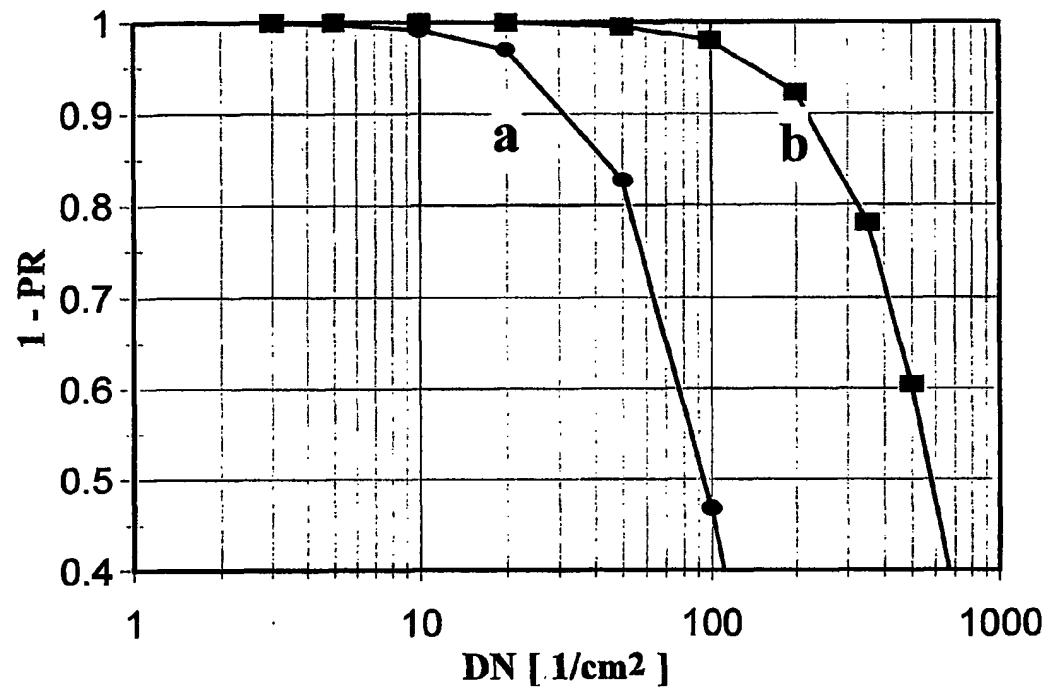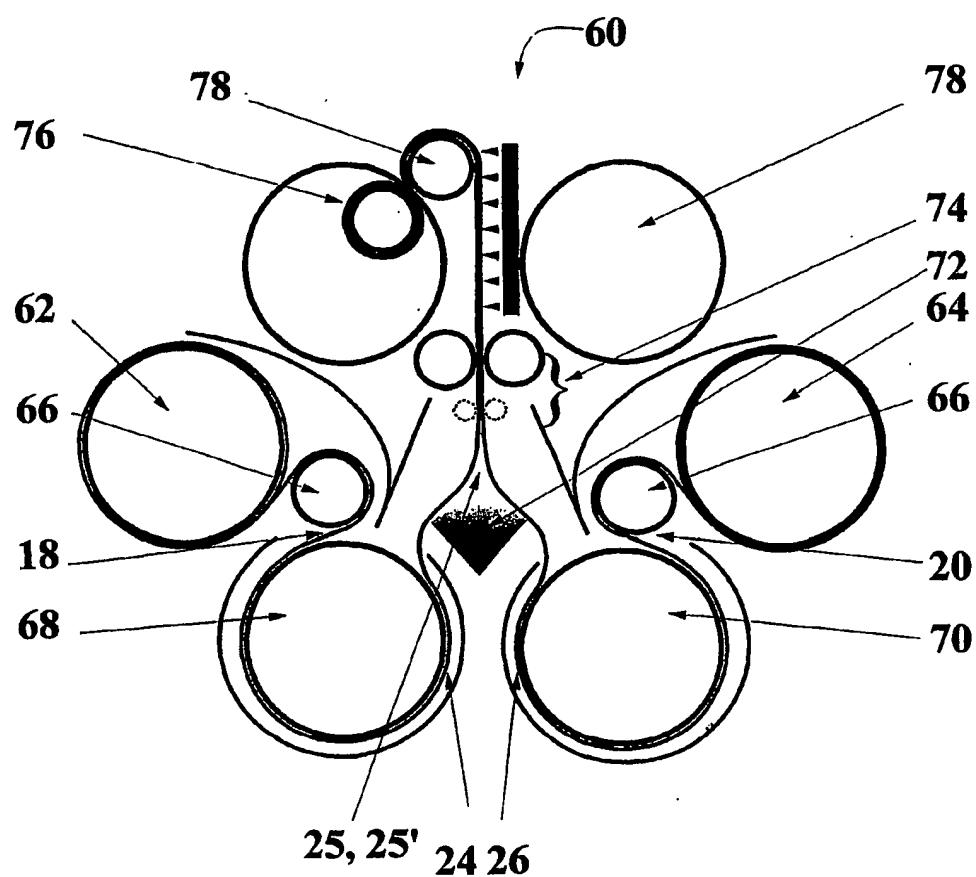
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Fig. 1.

Fig. 2.

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Fig. 3.

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50   52

54   56   58

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Fig. 4.

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Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01L51/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01L H05B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 65670 A (DU PONT) 2 November 2000 (2000-11-02)	1-3,5-9, 12, 14-17, 19,20, 22-26, 28,30-33
	page 6, line 18-22 page 16; example 4	
A		10,11, 13,27, 29,35,36
A	WO 00 36665 A (BATTELLE MEMORIAL INSTITUTE) 22 June 2000 (2000-06-22)	1-4, 7-12, 15-21, 24-28, 31-56
	page 9, line 29-31; table 1	

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| X | Further documents are listed in the continuation of box C. | X | Patent family members are listed in annex. |

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 August 2002	02/09/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	De Laere, A

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DA SILVA SOBRINHO A S ET AL: "TRANSPARENT BARRIER COATINGS ON POLYETHYLENE TEREPHTHALATE BY SINGLE-AND DUAL-FREQUENCY PLASMA-ENHANCED CHEMICAL VAPOR DEPOSITION" JOURNAL OF VACUUM SCIENCE AND TECHNOLOGY: PART A, AMERICAN INSTITUTE OF PHYSICS. NEW YORK, US, vol. 16, no. 6, November 1998 (1998-11), pages 3190-3198, XP000803453 ISSN: 0734-2101 the whole document	1,16,19

INTERNATIONAL SEARCH REPORT
Information on patent family members

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WO 0036665	A	22-06-2000	US	6268695 B1	31-07-2001
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			US	2001015620 A1	23-08-2001

Organic electronics: Introduction

by J. M. Shaw
P. F. Seidler
Guest Editors

For the past forty years *inorganic* silicon and gallium arsenide semiconductors, silicon dioxide insulators, and metals such as aluminum and copper have been the backbone of the semiconductor industry. However, there has been a growing research effort in "organic electronics" to improve the semiconducting, conducting, and light-emitting properties of *organics* (polymers, oligomers) and hybrids (organic–inorganic composites) through novel synthesis and self-assembly techniques. Performance improvements, coupled with the ability to process these "active" materials at low temperatures over large areas on materials such as plastic or paper, may provide unique technologies and generate new applications and form factors to address the growing needs for pervasive computing and enhanced connectivity.

If we review the growth of the electronics industry, it is clear that innovative organic materials have been essential to the unparalleled performance increase in semiconductors, storage, and displays at the consistently lower costs that we see today. However, the majority of these organic materials are either used as sacrificial stencils (photoresists) or *passive* insulators and take no *active* role in the electronic functioning of a device. They do not conduct current to act as switches or wires, and they do not emit light.

For semiconductors, two major classes of passive organic materials have made possible the current cost/performance ratio of logic chips: photoresists and insulators. Photoresists are the key materials that define chip circuitry and enable the constant shrinking of device dimensions [1–3]. In the late 1960s, photoresist materials limited the obtainable resolution of the optical tools to

~5.0 μm (~500 transistors/cm^2). As optical tools continued to improve, owing to unique lens design and light sources, new resists had to be developed to continue lithographic scaling. Chemists created unique photosensitive polymers to satisfy the resolution, sensitivity, and processing needs of each successive chip generation, and now photoresist materials improve the resolution that could normally be provided on an optical exposure tool. The increased resolution capability of photoresists combined with optical tool enhancements has enabled the fabrication of 1.2 million transistors/cm^2 with feature sizes of 180 nm, significantly smaller than the 248-nm exposure wavelength of the current optical exposure tool—an achievement that was not considered possible a few years ago.

Polymeric insulators have also been essential to the performance and reliability of semiconductor devices. They were first used in the packaging of semiconductor chips, where low-cost epoxy materials found applications as insulation for wiring in the fabrication of printed wiring boards and as encapsulants to provide support/protection and hence reliability for the chips [4, 5]. Although the first polymeric dielectrics were used in the packaging of chips, IBM recently introduced a polymer that replaces the silicon dioxide dielectric typically used on-chip throughout the industry as an insulator. The seven levels of metal wiring required to connect the millions of transistors on a chip can significantly affect chip performance because of signal propagation delay and crosstalk between wiring. Improvement in interconnect performance requires reduction of the resistance (R) and capacitance (C). IBM was the first to use copper to replace aluminum wiring as a low-resistivity metal, and the first to use a low-k

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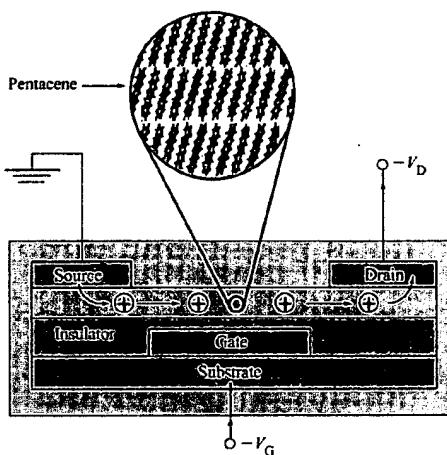
Figure 1

Schematic of organic semiconducting p-type thin-film transistor with top contacts.
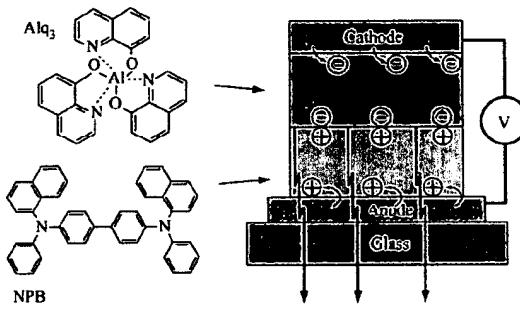
Figure 2

Schematic of typical organic light-emitting diode which uses Alq$_3$, tris(8-hydroxyquinolinato)aluminum, as the electron transport and emitting layer, and NPB, N,N'-di(naphthalene-1-yl)-N,N'diphenyl-benzidine, as the hole transport layer.

Figure 3

Performance of organic and hybrid semiconductors.

polymeric material, SiLK** [6] to replace typically used oxide insulators, thereby improving the total interconnect wiring performance by ~37%. With continued innovation in materials and design, it is felt that the on-chip wiring will not be a performance limiter for the next decade [7].

Organic materials have also provided performance and reliability for storage products and displays. The density of magnetic storage has increased at a faster rate than even semiconductor devices. Innovations in lubricants, thin-film head materials, and magnetic media have led to these advances. Similarly, the resolution of active-matrix liquid crystal displays (AMLCDs) is approaching photographic quality. The development of liquid crystals, fundamental understanding of alignment layers, and color filters using innovative dyes have contributed to the recent announcement of the IBM "Bertha" display with 200-dpi resolution and wide viewing angle [8].

The ability of chemists to optimize the properties of the organic materials described above has provided key contributions to the growth of the electronics industry. However, it is possible that within the next ten years we may reach the limits of performance improvements in silicon devices, magnetic storage, and displays that can be provided at a reasonable cost. As in the past, basic research on materials may provide a path to new product form factors.

Therefore, it is fitting that this issue of the *IBM Journal of Research and Development* for the first official year of the 21st century should be dedicated to organic electronics. Nontraditional materials such as conjugated organic molecules, short-chain oligomers, longer-chain polymers, and organic–inorganic composites are being developed that emit light, conduct current, and act as semiconductors. The ability of these materials to transport charge (holes and electrons) due to the π-orbital overlap of neighboring molecules provides their semiconducting and conducting properties. The self-assembling or ordering of these organic and hybrid materials enhances this π-orbital overlap and is key to improvements in carrier mobility. The recombination of the charge carriers under an applied field can lead to the formation of an exciton that decays radiatively to produce light emission. (Schematics of semiconducting and light-emitting devices are provided in **Figures 1 and 2.**) In addition to their electronic and optical properties, many of these thin-film materials possess good mechanical properties (flexibility

4

Semiconductor	Representative chemical structure	Mobility $(cm^2 V^{-1} s^{-1})$
Silicon	Silicon crystal	300–900
	Polysilicon	50–100
	Amorphous silicon	~1
Pentacene		~1
α,ω-dihexyl-sexithiophene		10^{-1}
α,ω-dihexylanthra-dithiophene		10^{-1}
Regioregular poly(3-hexylthiophene)		10^{-1}
Organic–inorganic hybrid	Phenethylamine–tin iodide	~1
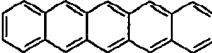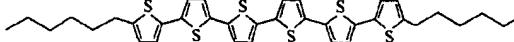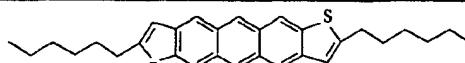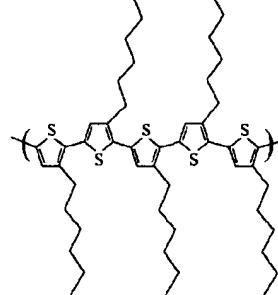
Figure 4

Chemical structures and comparison of mobilities of classes of organic and inorganic semiconductors.

and toughness) and can be processed at low temperatures using techniques familiar to the semiconducting and printing industries, such as vacuum evaporation, solution casting, ink-jet printing, and stamping. These properties could lead to new form factors in which roll-to-roll manufacturing could be used to create products such as low-cost information displays on flexible plastic, and logic for smart cards and radio-frequency identification (RFID) tags.

Efforts on these "active" materials initiated in academia and in industrial research laboratories in the 1970s and 1980s have led to a dramatic improvement in performance due to innovative chemistry and processing, as well as the growing ability to understand and control the self-assembly and ordering of oligomers, polymers, and nanocrystals. Research efforts on semiconducting conjugated organic thiophene oligomers [9, 10], thiophene polymers [11–13], and the small pentacene molecule [14–17] have led to improvements in the mobility of these materials by five orders of magnitude over the past 15

years, as shown in Figure 3. Figure 4 shows the chemical structures and reported mobilities of representative classes of organic materials compared to those of inorganic silicon materials. An overview of these materials and associated references are presented in the paper by Dimitrakopoulos and Mascaro in this issue. As each material appears to reach its limit in mobility and saturate in performance, another improved system takes its place. As seen in Figure 4, evaporated films of pentacene have achieved mobilities comparable to that of the amorphous silicon used to fabricate the thin-film transistors (TFTs) which drive the liquid crystal pixels in AMLCD flat-panel displays. Recently a new class of materials, organic–inorganic perovskites [18], has also achieved the mobility of amorphous silicon [19]. While these carrier mobilities are now useful for applications that do not require high switching speeds, all of the previously reported materials operated at high voltages. A method of providing low-voltage operation of these materials was

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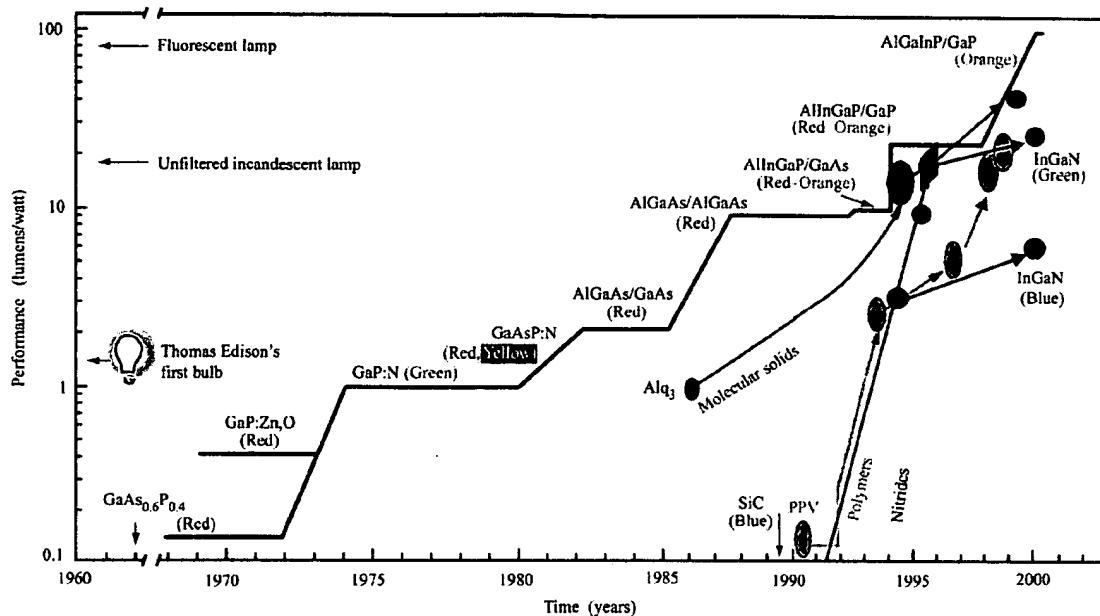
Figure 5

Evolution of LED/OLED performance. (Reprinted with permission from [24]; © 1996 American Association for the Advancement of Science.)

recently reported [16], enabling applications for portable electronics where battery lifetime is a concern.

Since these organic materials and hybrids are polycrystalline, it will be difficult to achieve the mobility of the single-crystal silicon used in high-performance microprocessors. Measurements on single organic crystals of p-type pentacene [17] and an n-type perylene [20] which mark the upper boundary of performance show mobilities of 2.7 cm^{2}V^{-1}s^{-1} and 5.5 cm^{2}V^{-1}s^{-1}—orders of magnitude lower mobility than single-crystal silicon. However, the organic–inorganic perovskites have demonstrated a Hall mobility of 50 cm^{2}V^{-1}s^{-1}, providing a possible path to increased performance [21].

The majority of these semiconducting organic materials are p-type, transporting holes (h$^+$) rather than electrons. While this journal issue focuses on p-type materials, n-type systems are also of interest because they enable the fabrication of p–n junctions, and complementary logic. Some examples have recently been reported in the literature [22, 23].

Further research is needed to improve the mobility and environmental stability of n-type and p-type materials, as well as a fundamental understanding of electron injection, metal contact issues, electron transport, surface modification, and self-assembly. However, organic systems

offer a great deal of flexibility in their synthesis, and as chemists develop new materials and learn how to better order and process them, it is hoped that mobility will continue to improve, perhaps reaching the performance of polysilicon and expanding the applications of such materials for low-cost logic chips.

Similar enhancements in performance have been seen in the development of organic light-emitting diodes (OLEDs). Figure 5 shows the dramatic increase in luminous efficiency of light-emitting molecular solids and polymers compared to typical inorganic LEDs over a 15-year time scale. Pioneering work was done at Eastman Kodak in 1987 on evaporated small molecules [25] and at Cambridge University in 1990 on solution-processed semiconducting polymers [26]. Currently, the highest observed luminous efficiencies of derivatives of these materials exceed that of incandescent lightbulbs, thus eliminating the need for the backlight that is used in AMLCDs.

The electronic and optical properties of these "active" organic materials are now suitable for some low-performance, low-cost electronic products that can address the needs for lightweight portable devices for the 21st century. This special issue of the *IBM Journal of Research and Development* provides the reader with information

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on the status and applications of organic and hybrid conducting, semiconducting, light-emitting, and magnetic materials. The first four papers demonstrate how the synthesis, ordering, and self-assembly of new materials can give rise to improved electronic, optical, and magnetic properties.

The first paper, by Dimitrakopoulos and Mascaro, reviews efforts on organic semiconducting materials, fabrication processes, device designs, and applications, with an emphasis on IBM activities during the last four years. The authors point out that organic semiconductors are limited by the weak van der Waals interactions between molecules, since at room temperature their vibrational energy approaches that of their intermolecular bond energies. Therefore, it may be difficult to further improve the current set of organic semiconductors. However, the next paper, by Mitzi, Chondroudis, and Kagan, reviews the unique electronic and optical properties that have been observed in a new class of materials—organic–inorganic hybrids. These materials offer the potential of improved transport because the inorganic portion of the hybrid material provides stronger covalent or ionic bonds compared to the weaker intermolecular interactions in organic semiconductors, while the organic portion of the system provides the required processibility and mechanical properties.

The paper which follows, by Murray et al., describes the synthesis of a different type of organic–inorganic hybrid: a colloidal nanocrystal. It consists of an inorganic core coordinated with an organic monolayer, which provides monodisperse building blocks that self-assemble into ordered superlattices. By tailoring the size and composition of the inorganic core, and the length and chemical functionality of the organic capping layer, the electronic [27], optical, and magnetic [28] properties of these materials can be studied as a function of size, perhaps providing a fundamental understanding of the limits of scaling for storage and semiconductors.

The paper by Angelopoulos provides an overview of applications for conducting polymers in the microelectronics industry, with a focus on polyaniline. Until the 1970s, the majority of polymers were classified and used as insulating materials. However, in 1978 it was discovered that electrons could be added or subtracted (chemical doping) from unsaturated polymers such as polyacetylene, polythiophenes, and polyanilines, allowing the flow of current [29]. This opened an entire new field, and for their discovery and development of conducting polymers, Alan Heeger, Alan MacDiarmid, and Hideko Shirakawa were awarded the Nobel Prize in Chemistry last year. These conducting polymers have unique properties in that they combine the electronic properties of metal with the processability and mechanical properties of polymers. While they are still orders of magnitude less conducting

than copper, they are useful for many applications, such as coatings for electrostatic discharge protection, corrosion protection, and electrodes for metallization. Advances in synthesis and ordering or self-assembly of these materials are expected to yield significant improvements in conductivity.

The development and optimization of new organic systems requires innovative methods, techniques, and computer simulation to provide fundamental understanding of charge injection and transport, and to guide the optimization and development of novel materials.

The next three papers provide the fundamental understanding needed to optimize the performance of small-molecule organic light-emitting devices. The paper by Riess et al. investigates the influence of trapped and interfacial charges, showing that the delay time for the onset of electroluminescence at low voltages is controlled by the buildup of internal space charges, which facilitates electron injection, rather than by charge-carrier transport through the organic layers. In general, the control of internal barriers in multilayered structures is key to tailoring device performance. The paper by Alvarado et al. is an overview of spectroscopy and electroluminescence excitation experiments with a scanning tunneling microscope (STM) to study the physical and electronic structures of the organic materials used in OLEDs. Here the role of the top electrode in an OLED is played by the STM tip. Charge carriers are injected from the tip into the organic stack to provide information on emission homogeneity, degradation of emission, energy barriers, carrier mobility, and recombination efficiency. The STM, which was invented in 1982 [30], allowing investigators to "see" at a molecular level, continues to be a key enabler providing fundamental information on the performance limitations of OFETs and OLEDs.

The paper by Curioni and Andreoni describes the use of computer simulations to study $tris$(8-hydroxyquinolato)aluminum (Alq_3), the prototypical electron-transporting and -emitting material used in OLEDs, and its interaction with the metals typically used as cathodes. The work is aimed at gaining insight into the electronic properties of the solid phase of Alq_3, as seen in Figure 2. The authors propose new derivatives that may have higher intrinsic luminescence.

The last paper, contributed by Howard and Prache from eMagin Corporation, discusses the use of OLEDs for microdisplay applications. Microdisplays, which exploit the dense electronic circuitry in a silicon chip, are providing a new wave of ultraportable information products, including headsets for viewing movies and cellular phones with full-screen Internet access. The requirements for these displays are reviewed, and a case is made to show that OLEDs are the best candidate for transducer technology.

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The electronics industry must satisfy the demands of an increasingly complex society for pervasive computing: access to instant information, data handling, and communication. Although organic electronics is a new area, the performance improvements in OLEDs and in organic conducting and semiconducting materials have generated much commercial interest. An OLED material has already led to a commercial product, an automobile display available from Pioneer. In addition, companies such as Eastman Kodak in collaboration with Sanyo Electric, Cambridge Display Technologies together with Seiko Epson, E-Ink in conjunction with Lucent, TDK, Philips Electronics, eMagin, Dupont/Uniax, Covion Organic Semiconductors, Idemitsu Kosan, and Plastic Logic, to name only a few, are developing products and obtaining intellectual property in the field.

There will be continued growth in the field of organic electronics, fueled by the promise of the new products and applications that can be derived from electronically and optically active organic and hybrid materials. These include low-cost and perhaps even flexible displays for e-newspapers and advertising, and low-cost memory and logic devices. Long-term research efforts and innovation are needed to provide new organic semiconductors, organic light-emitters, and conducting polymers with improved performance, processability, and environmental stability to oxygen and moisture. The successful development of these new materials will require increased multidisciplinary partnerships among physicists, chemists, biochemists, and engineers. As improvements in material properties are realized over the next ten years, organic electronics may displace traditional entrenched technologies and manufacturers.

We wish to thank the contributing authors for their enthusiasm for this issue, and all the referees who dedicated time to review these papers. In addition we would like to thank Homer Antoniadis at OSRAM Opto Semiconductors, Inc., and Margaret Cargiulo, Christos Dimitrakopoulos, Patrick Malenfant, and Walter Riess at IBM Research for their graphics assistance; a special thanks to David Mitzi and Tom Jackman for the graphic of an organic–inorganic hybrid semiconductor shown on the front cover of this journal.

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Organic electroluminescent diodes

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A novel electroluminescent device is constructed using organic materials as the emitting elements. The diode has a double-layer structure of organic thin films, prepared by vapor deposition. Efficient injection of holes and electrons is provided from an indium-tin-oxide anode and an alloyed Mg:Ag cathode. Electron-hole recombination and green electroluminescent emission are confined near the organic interface region. High external quantum efficiency (1% photon/electron), luminous efficiency (1.5 lm/W), and brightness (> 1000 cd/m^2) are achievable at a driving voltage below 10 V.

Organic materials have previously been considered for the fabrication of practical electroluminescent (EL) devices.[1] The primary reason is that a large number of organic materials are known to have extremely high fluorescence quantum efficiencies in the visible spectrum,[2,3] including the blue region, some approaching 100%. In this regard, they are ideally suited for multicolor display applications.

However, the development of organic EL devices has not been successful so far, one reason being that high voltage is generally required to inject charges into organic crystals (e.g., anthracene). In early attempts by Helfrich and Schneider,[4] Dresner,[1] and Williams and Schadt,[5] the drive voltage was on the order of 100 V or above in order to achieve a significant light output. Therefore, the EL device power-conversion efficiency is quite low, typically less than 0.1% W/W, despite the reported high external quantum efficiency of ~5% photon/electron. In an attempt to reduce the drive voltage, Vincett et al.[6] used thin organic films of similar materials in their EL devices. They reported EL operation below 30 V. However, the quantum efficiency of their EL diodes was only about 0.05%, presumably owing to the inefficiency of electron injection and the inferior quality of the evaporated anthracene films. Other organic thin-film EL work[7,8] reported similar performance. Another factor for the lack of development is perhaps the question of long-term stability of organic EL diodes. There are very few reported data on the organic EL stability in the literature.[6]

In this letter, we report a novel thin-film organic device with superior EL characteristics. It is efficient and can be driven to high brightness by a low dc voltage. In contrast to most organic EL cells, which use a single layer of organic material sandwiched between two injecting electrodes, our EL diode consists of a double layer of organic thin films, with one layer capable of only monopolar transport. The organic materials were chosen such that the morphological, transport, recombination, and luminescent properties were compatible with the construction and operation of the thin-film EL diodes. In addition, we used a low-work-function alloy prepared by vapor codeposition as the cathode for efficient electron injection.

Figure 1 shows the structure of the present EL cell. The substrate is an indium-tin-oxide (ITO) coated glass with a sheet resitance of about 10–20 Ω/□ (Nesatron™ from PPG Industries). It was cleaned by ultrasonication in a mixture of isopropyl alcohol and water (1:1) and degreased in toluene vapor. The first organic layer (about 750 Å) on top of the substrate is an aromatic diamine[9] of molecular structure shown in Fig. 1. The second organic layer is the luminescent film, about 600 Å. It belongs to a class of fluorescent metal chelate complexes.[10] The specific example shown in Fig. 1 is 8-hydroxyquinoline aluminum (Alq$_3$). The top electrode is an alloy or mixture of magnesium and silver with an atomic ratio of 10:1. The organic layers, as well as the Mg:Ag electrode, were all deposited by vacuum deposition (~10^{-5} Torr). The substrate was nominally at room temperature and the deposition rates for the organic layers were about 2–5 Å/s. The Mg:Ag electrode was deposited by simultaneous evaporation from two separate sources at a total rate of about 10 Å/s.

The organic diode shown in Fig. 1 can be operated in a continuous dc or pulsed mode. It behaves like a rectifier, the forward bias corresponding to a positive voltage on the ITO electrode. Light emission, seen only in forward bias, was measurable from as low as about 2.5 V. Figure 2 shows the continuous dc current vs voltage (I-V) and the radiance exitance vs voltage (B-V) curves. The shape of the I-V curves for most diodes is relatively independent of the thickness of the diamine layer but strongly dependent on that of the Alq$_3$ layer, indicating that most of the bias voltage is across the Alq$_3$ layer. The I-V curve can be fitted to an injection-limited model where the electron current is limited by electron emission from the cathode into the Alq$_3$ layer. The radiance exitance in mW/cm^2 was measured from a diode with an emit-
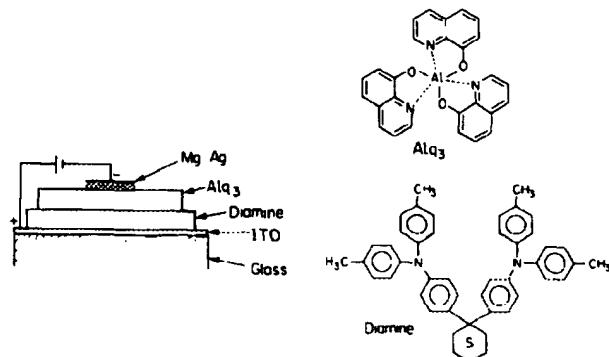

FIG. 1. Configuration of EL cell and molecular structures.
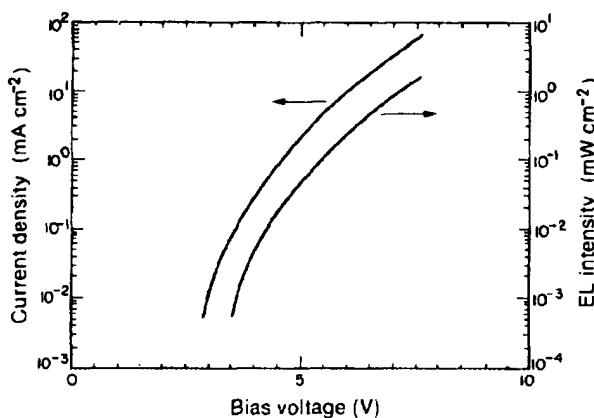
FIG. 2. Brightness-current-voltage characteristics of an ITO/diamine/Alq₃/Mg:Ag EL cell.

ting area of 0.1 cm² by a radiometer (EGG model 550-1). The emitting surface is Lambertian for viewing angles within 60° from the normal to the surface. The brightness in units of cd/m² was separately measured by a spot photometer (Minolta Luminance Meter, $nt - 1/3°$). A radiance exitance of 0.1 mW/cm² is equivalent to a brightness of 100 cd/m² for the EL diode with Alq₃ as the emitter. As shown in Fig. 2, the EL diode can be driven to produce high brightness (> 1000 cd/m²) with a dc voltage of less than 10 V. In pulsed operation, the response of the diode has a rise and decay time on the order of a few microseconds.

The light output from the EL diode is linearly proportional to the input current in the current range from 10^{-1} to 10^2 mA/cm². The external quantum efficiency of the EL diode is about 1%. At the power output of 0.1 mW/cm², which is visible in ambient lighting, the required drive voltage is 5.5 V and the corresponding power conversion efficiency is 0.46%. The equivalent luminous efficiency is 1.5 lm/W, which compares favorably with the commercially available light-emitting diodes or ZnS-based EL devices.[11]

The emission spectrum of the EL diode is shown in Fig. 3. The peak intensity is at 550 nm, the FWHM is about 100 nm, and the color is green. The EL emission spectrum is independent of the drive voltage or current but is sensitive to the thickness of the organic layers. The latter effect is due to the interference phenomenon of emission in front of a reflecting mirror.[12] For thin organic films (as in Fig. 1) the EL
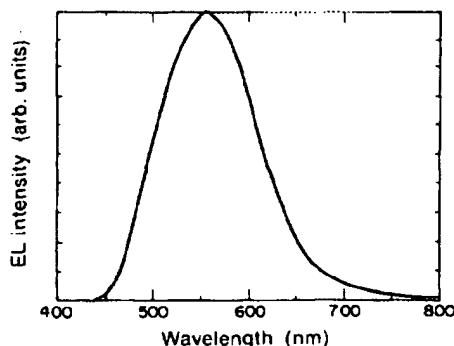
emission spectrum is identical to the photoluminescence spectrum of the Alq₃ thin film. This result indicates that the radiative recombination of injected electrons and holes takes place in the Alq₃ layer. Detailed analysis[11] shows that this recombination is confined to the Alq₃ layer adjacent to the diamine layer to a distance of about 300 Å. The diamine layer, which is known to transport holes only,[9] blocks the electrons injected from the Mg:Ag electrode. Therefore, the interface between the diamine and Alq₃ layer effectively controls the recombination processes.

The morphological properties of the organic layers are critical in the construction of thin-film devices without pinholes. It is necessary that both layers in the EL device be smooth and continuous. The transmission electron micrographs show that the evaporated diamine layer appears to be amorphous, whereas the Alq₃ film is microcrystalline with an average grain size of about 500 Å. The ability to form smooth films in both layers in the present EL diode is related to the low order of symmetry as well as large molecular geometry of the constituent molecules. In addition, the two-layer structure partially alleviates the shorting problem by minimizing the probability of having overlapping pinholes.

The Mg:Ag alloy used as the cathode is important in the reduction of the drive voltage. Mg is a low-work-function metal ideally suited for electron injection into organic materials. However, it is susceptible to atmospheric oxidation and corrosion. The incorporation of Ag in the Mg:Ag film is found to retard these degradation processes. In addition, Ag improves the sticking coefficient of Mg on the organic film during vapor deposition. Other common cathode materials such as In, Ag, and Al generally result in much higher voltage drive and inferior stability.

The EL diode has been tested for stability in a continuous dc operation. Under constant current drive of 5 mA/cm² and in an argon ambient, the EL emission (with initial output of about 0.05 mW/cm² or 50 cd/m²) shows a relatively fast degradation in the initial hours (about 30% loss in 10 h) and then decays at a much slower rate to about half of the initial value at the end of a 100-h test. The steady degradation is accompanied by a concomitant increase in the drive voltage from the initial 6 or 7 V to about 14 V during this test period. The nature of degradation is not clearly understood. Some of the failure is attributed to the degradation of both hole and electron injecting contacts, the latter resulting in the formation of dark nonemissive spots.

In conclusion, we have shown a novel organic electroluminescent diode with a double-organic-layer structure. The diode has unique characteristics of high electroluminescent emission efficiency, fast response, low voltage drive, and simplicity of fabrication. It demonstrates that organic materials can indeed be viable alternatives for optoelectronic applications such as displays.

FIG. 3. Electroluminescence spectrum of ITO/diamine/Alq₃/Mg:Ag.

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